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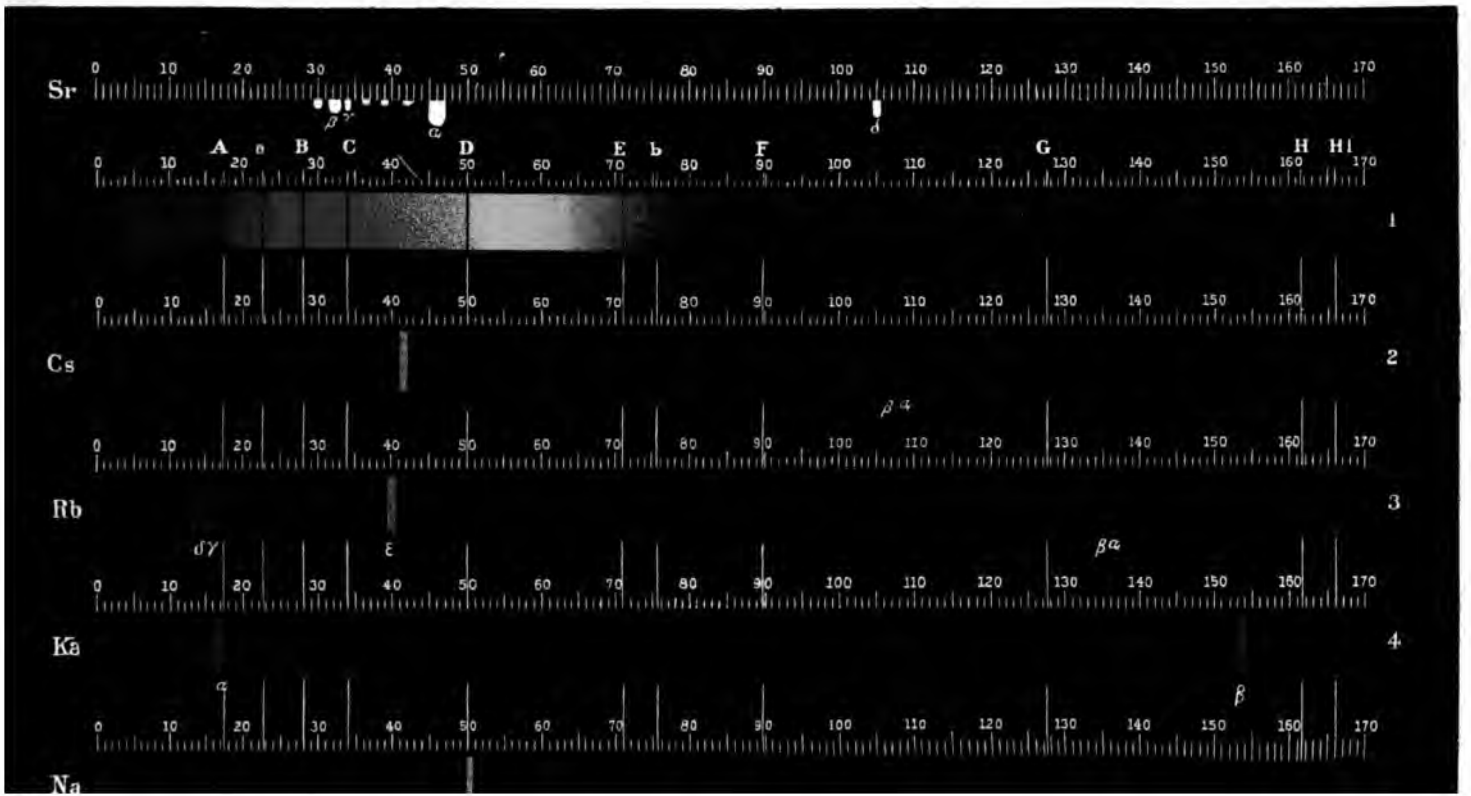
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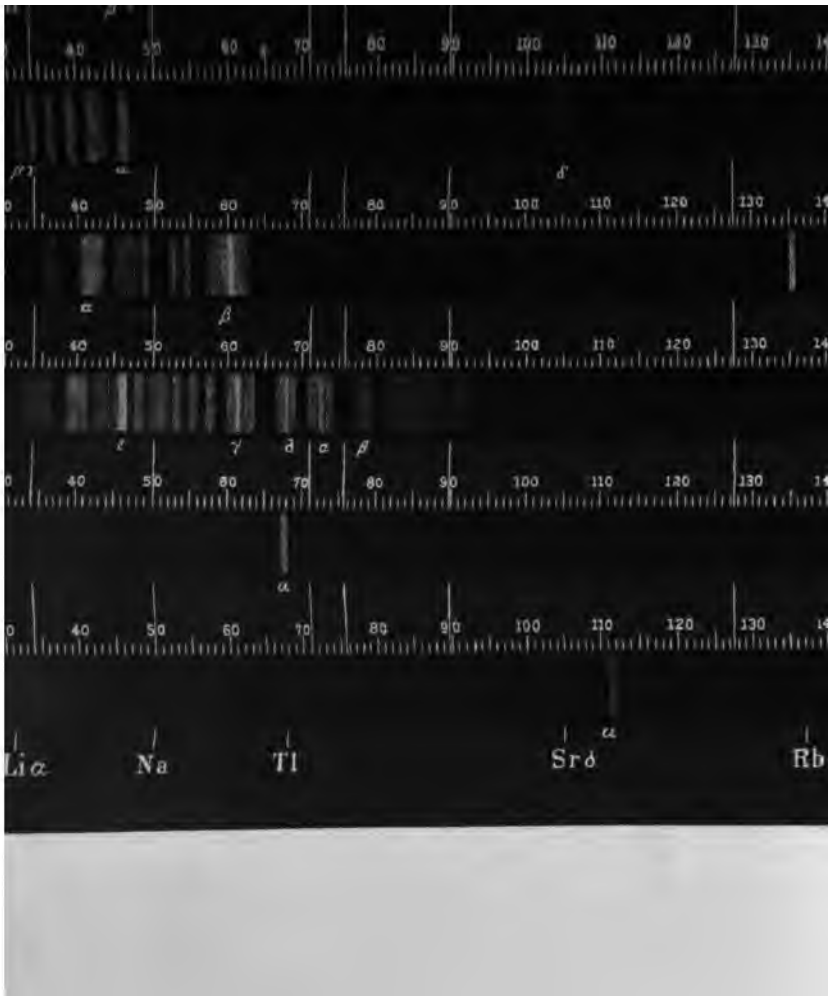
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α
Rb

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PREFACE.

During the fourteen years that have elapsed since the appearance of the last American edition of this work, two revised German editions (the fifteenth and sixteenth) have been published, embracing so many additions and other improvements that the need of a new translation has been felt. With the consent of the author (given only a few months before his death), and also with the permission of Prof. S. W. Johnson, editor of the preceding American editions, this translation has therefore been undertaken.

Except in regard to nomenclature and chemical formulas, the present work faithfully represents the recent sixteenth German edition. The example of the previous American issue has been followed in giving modern chemical formulas (Fresenius, in recent editions, has given both old and new), and in modernizing the greater part of the nomenclature. The few additions made to the text are enclosed in brackets in nearly all cases.

The translator has followed the author in avoiding the introduction of abbreviated analytical tables, believing that such tables are often stumbling-blocks in the way of an intelligent study of the subject.

As far as possible, use has been made of the text of the last American edition, but the changes and additions in the German work have been so extensive that it has been necessary to rewrite a large part of the matter, and to reset the type for the whole work. Previous condensations and omissions have been here restored, and larger and smaller type, also, have been used in the same way as in the German edition.

The translator trusts that the care bestowed upon the

31306

work, in the effort to insure accuracy of statement and clearness of language, will make the present edition satisfactory to those who use it; and he desires to acknowledge the valuable assistance, in proof-reading, of Miss Lucy P. Bush, of New Haven.

In view of the recent death of the author, it seems appropriate to give, at this time, some facts concerning the history and development of the work, as described in the prefaces to the German editions.

While a student at Bonn, in the winter of 1840–1, Fresenius wrote out a course of qualitative analysis, merely for the sake of practice. Following the advice of an experienced chemist, whose name is not given, he published these notes, thus issuing the first edition of his "Qualitative Analysis." In the spring of 1841, he became assistant, and afterwards instructor (Privatdocent), in Liebig's laboratory at Giessen, and occupied himself there with the instruction of beginners in chemical analysis. A second edition of the work appeared in 1842, with a preface of recommendation by Liebig. The latter stated that the book contained many new and simplified methods of separation, so that it would be welcomed even by those who possessed the larger works on mineral analysis. At this time, the systematic course was preceded by a descriptive part relating to reactions, thus making the treatise an independent one. This edition was translated into Dutch, English, French, and Italian, and was used in many prominent laboratories. A third edition was published in 1844, while the author was still at Giessen.

In the autumn of 1845, Fresenius removed to Wiesbaden, which was to be his home for the rest of his life. At first he was Professor of Chemistry, etc., at the Agricultural Institute, and during this period of somewhat more than two years the fourth and fifth editions of the book appeared. These issues, besides being revised and otherwise improved, contained an additional section, devoted to the reactions and detection of the more important vegetable alkaloids.

In the position just mentioned, Fresenius was unable to carry on his favorite task of teaching analytical chemistry to young men, so that in the spring of 1848, he opened an independent laboratory for instruction. This developed into the

important institution which is still in operation. The author's work now enabled him to observe continually the use of his book in the hands of large numbers of students, and, under these favorable conditions, the remaining editions, from the sixth to the sixteenth, have appeared.

To the seventh edition was added a section relating to courses of analysis in special cases, thus increasing the utility of the work for those engaged in practical investigations. In the preface to the ninth edition, the author stated that he had always remained true to the firm principle, never to admit anything into his work without personal verification. In the eleventh edition, of 1862, the recently discovered spectroscopic reactions were included, and, for the first time, the work was made to embrace all the known elements. The twelfth, thirteenth, and fourteenth editions contained few changes, but the fifteenth, published in 1885, was thoroughly revised, and formulas of the new system (in addition to those of the old) were introduced. The last (sixteenth) edition, which appeared ten years later, was also completely revised. A new feature was introduced at this time by the insertion of a much larger number of references to chemical literature, relating especially to additional methods. The usefulness of the work was thus considerably enhanced, without unduly increasing its size.

H. L. W.

New Haven, Conn., September, 1897.

NOTE.

All temperatures mentioned in this book refer to degrees of the Centigrade thermometer.

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INTRODUCTORY.

PRELIMINARY REMARKS.

It is well known that chemistry is the science which teaches us to understand the substances of which our earth consists, their composition and manner of decomposition, and especially their behavior towards one another. A special branch of this science is designated by the name *analytical* chemistry, inasmuch as it pursues a certain object, which is the breaking up (the analysis) of compound bodies and the discovery of their constituents. In this investigation of the constituents, if consideration is taken only of their *kind*, the analysis is a *qualitative* one; but if the *amount* of each substance is investigated, it is a *quantitative* one. The office of *qualitative* analysis is to exhibit the constituent parts of a substance of *unknown* composition in forms of *known* composition, from which the constitution of the body examined, and the presence of its several component elements, may be positively inferred. The efficiency of its method depends upon two conditions, viz., it must attain the object in view with unerring certainty and in the most expeditious manner. The object of quantitative analysis, on the other hand, is to exhibit the elements revealed by the qualitative investigation in forms which will permit the most accurate estimate of their weight, or to effect by other means the determination of their quantity.

The means by which these different ends are reached present wide variations in the two cases. The study of quali-

tative analysis must, therefore, be pursued separately from that of quantitative analysis, and must naturally precede it.

The idea and aim of qualitative analysis in general having thus been stated, consideration must next be given to the preliminary knowledge which warrants its pursuit, the rank which it takes in the domain of chemistry, the objects to which it is applied, and its use; then the chief points upon which its study depends, and the principal divisions into which it is separated must, also be considered.

For the successful pursuit of qualitative investigations, it is absolutely indispensable that the student should possess some knowledge of the chemical elements and of their most important combinations, as well as of the principles of chemistry in general, and that he should combine with this knowledge some readiness in the comprehension of chemical processes. The practical part of this science demands, moreover, strict order, great neatness, and a certain skill in manipulation. If the student joins to these qualifications the habit of invariably ascribing the failures with which he may meet to some error or defect in his operations, or, in other words, to the absence of some condition indispensable to the success of the experiment—and a firm reliance on the immutability of the laws of nature cannot fail to create this habit —he possesses every requisite to render his study of analytical chemistry successful.

Although chemical analysis is based on general chemistry, and cannot be properly pursued without some knowledge of the latter, yet we have to look upon it as one of the main pillars upon which the entire structure of the science rests, since it is of almost equal importance for all branches of theoretical as well as of practical chemistry; and the use which it affords to the practical chemist, the mineralogist, and the metallurgist, to the pharmacist, the physician, the rational agriculturist, and others, needs no explanation.

These considerations would furnish sufficient reason for recommending a thorough study of this branch of science, even if its cultivation lacked those attractions which it possesses for every one who devotes himself ardently to it. The mind is constantly striving for the attainment of truth; it delights in the solution of problems, and where do we meet with

a greater variety of them, more or less difficult of solution, than in the province of chemistry? But as a problem to which, after long pondering, we fail to discover the key wearies and discourages the mind, so do chemical investigations, if the object in view be not attained, if the results do not bear the stamp of unerring certainty. A *half-knowledge* is, therefore, to be considered worse than no knowledge; and a *superficial* cultivation of chemical analysis is to be particularly guarded against.

A qualitative investigation may be made with either of two objects in view, viz., 1st, to prove that a certain body is or is not contained in a substance, *e.g.*, lime in well-water; or, 2d, to ascertain *all* the constituents of a chemical compound or mixture. Any substance whatever may, of course, become the object of a chemical analysis.

Since, however, the elements are not all of equal importance in practical chemistry (as only a certain number of them occur widely distributed in nature, and are important in the manufacture of chemical preparations, in metallurgy, pharmacy, trade, the arts, manufactures, and agriculture; while the others are merely constituents of rare minerals), in order to facilitate the study of beginners and the work of practical chemists, only the more common elements and their more important compounds are treated in full detail in the present work. The rarer elements are treated more briefly, and in such a manner that they can be studied separately without difficulty.

The study of qualitative analysis may be properly divided into four principal parts:

1. Chemical operations.
2. Reagents and their uses.
3. Deportment of the various bodies with reagents.
4. Systematic course of qualitative analysis.

It will be readily understood that the pursuit of chemical analysis requires *practical skill and ability*, as well as *theoretical knowledge;* and that mere speculative study can as little lead to success as purely empirical experiments. To attain the desired end, theory and practice must be judiciously combined.

SECTION I.

OPERATIONS.

§ 1.

THE operations of analytical chemistry are essentially the same as those of synthetical chemistry, though modified to a certain extent to adapt them to the different object in view, and to the small quantities operated upon in analytical investigations.

The following are the principal operations in qualitative analysis:

§ 2.

1. SOLUTION.

The term *solution*, in its widest sense, denotes the union of a body, whether gaseous, liquid, or solid, with a fluid, resulting in a homogeneous liquid. When the substance dissolved is *gaseous*, the term *absorption* is more properly made use of, and the solution of one fluid in another is generally called a *mixture*. The term solution, in its usual sense, means the union of a *solid* body with a liquid.

A solution is more readily effected the more minutely the body to be dissolved is divided. The fluid by means of which the solution is effected is the *solvent*. We call the solution *chemical* where the solvent enters into chemical combination with the substance dissolved; and *simple*, where no definite combination takes place.

In a *simple* solution, the dissolved body is supposed to exist in the free state, and to retain all its original properties except those dependent on its form and cohesion, since it separates unaltered when the solvent is withdrawn. Common salt dissolved in water is a familiar instance of a simple solution. The salt imparts its peculiar taste to the liquid. On evaporating the water, the salt is left behind in its original

form. A simple solution is called *saturated* when the solvent contains all it can hold of the dissolved substance. But as fluids generally dissolve larger quantities of a substance the higher their temperature, the term *saturated*, as applied to *simple* solutions, is only relative, and refers invariably to a certain temperature. As a general rule, elevation of temperature facilitates and accelerates simple solution. This rule has but few exceptions.

A *chemical* solution contains the dissolved substance not in the same state nor possessed of the same properties as before. The dissolved body is intimately combined with the solvent, the latter having also lost its original properties. A new substance has thus been produced, and the solution, therefore, manifests the properties of this new substance. A chemical solution, also, may be usually *accelerated* by elevation of temperature, since heat generally promotes the action of bodies upon each other. The *quantity* of the dissolved body, however, always remains the same in proportion to a given quantity of the solvent, the combining proportions of substances being invariable and independent of the gradations of temperature.

The reason of this is that in a chemical solution the solvent and the body upon which it acts have more or less opposite properties, which tend to neutralize each other. Solution ceases as soon as this tendency is satisfied. In this case, also, the solution is said to be *saturated*, or, under certain conditions, *neutralized*, and the point which denotes it to be so is termed the point of saturation or neutralization.

The substances which produce chemical solutions are in most cases either acids or alkalies. With few exceptions they have first to be converted to the fluid state by means of a simple solvent. When the opposite properties of acid and base are mutually neutralized, and the new compound is formed, the actual transition to the fluid state will ensue only if the new compound possesses the property of forming a simple solution with the liquid present, *e.g.*, when a solution of acetic acid in water is brought into contact with lead oxide, there ensues, first, a chemical combination between the acid and the oxide, and then a simple solution of the newly formed lead acetate in the water present.

In chemical laboratories, solutions are generally made by digesting or heating the substance to be dissolved with the fluid in beaker-glasses, flasks, test-tubes, or capsules. In the preparation of chemical solutions, the best way usually is, in the first place, to mix the body to be dissolved with water (or with whatever other indifferent fluid may happen to be used), and then gradually add the chemical agent. By this course of proceeding, a large excess of the latter is avoided, an over-energetic action guarded against, the process greatly facilitated, and complete solution insured—which is a matter of some importance, as it frequently happens in chemical combinations that the product formed refuses to dissolve if an excess of the chemical solvent is present. In this case, the new salt first formed, being insoluble in the liquid present, gathers around and encloses the portion still unacted on, weakening thereby or preventing altogether further chemical action upon it. Thus, for instance, witherite (barium carbonate) dissolves readily when, after being reduced to powder, water is poured upon it and hydrochloric acid gradually added; but it dissolves with difficulty and imperfectly when projected into a concentrated solution of hydrochloric acid in water, for barium chloride will dissolve in water, but not in hydrochloric acid.

CRYSTALLIZATION and PRECIPITATION are the reverse of solution, since they have for their object the conversion of a fluid or dissolved substance to the solid state. As both generally depend on the same cause, viz., on the absence of a solvent, it is impossible to assign exact limits to either; in many cases, they merge into one another. We must, however, consider them separately here, as they differ essentially in their extreme forms, and as the special objects which we purpose to attain by their application are generally very different.

§ 3.

2. CRYSTALLIZATION.

We understand by the term crystallization, in a more general sense, every operation or process whereby bodies

are made to pass from the fluid to the solid state, and to assume certain fixed, mathematically definable, regular forms. But as these forms, which we call *crystals*, are usually more regular, and consequently more perfect, the more slowly the operation is carried on, we commonly connect with the term *crystallization* the accessory idea of a *slow* separation, of a *gradual* conversion to the solid state. The formation of crystals depends on the regular arrangement of the constituent particles of bodies (*molecules*). It can only take place, therefore, if these molecules possess perfect freedom of motion, and thus, in general, only when a substance passes from the fluid or gaseous to the solid state. Those instances in which the mere ignition or the softening or moistening of a solid body suffices to make the tendency of the molecules to a regular arrangement (crystallization) prevail over the diminished force of cohesion; for instance, the turning white and opaque of moistened barley-sugar, are to be regarded as exceptional cases.

To induce crystallization, the causes of the fluid or gaseous form of a substance must be removed. These causes are either *heat alone, e.g.*, in the case of fused metals; or *solvents alone*, as in the case of an aqueous solution of common salt; or *both combined*, as in the case of a hot saturated solution of potassium nitrate in water. In the first case, we obtain crystals by cooling the fused mass; in the second, by evaporating off the solvent; and in the third, by either of these means. The case occurring most frequently is that of crystallization by cooling hot saturated solutions. The liquids which remain after the separation of the crystals are called *mother-liquors*. The term *amorphous* is applied to such solid bodies as have no crystalline form.

We generally have recourse to crystallization either to obtain the crystallized substance in a solid form, or to separate it from other substances dissolved in the same liquid. In many cases, also, the form of the crystals or their deportment in the air, viz., whether they remain unaltered or effloresce or deliquesce upon exposure to the air, will afford an excellent means of distinguishing between bodies otherwise resembling each other; for instance, between sodium sulphate and potassium sulphate. The process of crystallization is usually

effected in dishes or, in the case of very small quantities, in watch-glasses.

Where the quantity of fluid to be operated upon is small, the surest way of getting well-formed crystals is to let the fluid evaporate in the air, or, better, under a bell-glass over an open vessel half filled with concentrated sulphuric acid. Minute crystals are examined best with a lens or microscope.

§ 4.

3. Precipitation.

This operation differs from the preceding one in that the dissolved body is *suddenly*, or at least more or less quickly, converted to the solid state, no matter whether the substance separating is crystalline or amorphous, whether it sinks to the bottom of the vessel, or ascends, or remains suspended in the liquid. Precipitation is caused either by a modification of the solvent—thus, calcium sulphate (gypsum) separates immediately from its solution in water upon the addition of alcohol—or in consequence of the separation of a body, formed by simple or double decomposition, which is insoluble in the liquid which is present. Thus, metallic copper is precipitated when a solution of copper chloride is brought into contact with zinc; a precipitation of calcium oxalate results when oxalic acid is added to a solution of calcium acetate; one of lead chromate is produced when dissolved potassium chromate is mixed with dissolved lead nitrate. In exchanges of this kind, one of the products generally remains in solution, as the zinc chloride, the acetic acid, and the potassium nitrate, in the instances just mentioned. Cases, however, may occur in which the newly formed substances are both precipitated, and nothing remains dissolved in the liquid. Such is the case, for instance, when a solution of magnesium sulphate is mixed with baryta-water, or when a solution of silver sulphate is precipitated with barium chloride.

Precipitation is resorted to for the same purposes as crystallization, viz., either to obtain a substance in the solid form, or to separate it from other dissolved substances. In qualitative analysis, however, we have recourse to this operation more

particularly for the purpose of detecting and distinguishing substances by the color, properties, and general deportment which they exhibit when precipitated either in an isolated state or in combination with other substances. The solid body separated by this process is called the *precipitate*, and the substance which acts as the immediate cause of the separation is termed the *precipitant*. Various terms are applied to precipitates by way of particularizing them according to their different nature, as crystalline, pulverulent, flocculent, curdy, gelatinous precipitates, etc.

Precipitates which appear simply pulverulent to the unaided eye can be seen not infrequently, when observed under the microscope, to consist entirely of very small, often very regular crystals, and in this manner, precipitates which are apparently alike can often be distinguished with ease and certainty.

The terms *turbid*, *turbidity*, or *cloudy* and *cloudiness*, are made use of to designate the state of a fluid which contains a precipitate so finely divided and so inconsiderable in amount that the suspended particles, although impairing the transparency of the fluid, cannot be clearly distinguished. The separation of flocculent precipitates may be generally promoted by vigorous shaking; that of crystalline precipitates, by stirring the fluid and rubbing the sides of the vessel in contact with the liquid with a glass rod. Elevation of temperature is also an effective means of promoting the separation of most precipitates. The process is conducted, according to circumstances, either in test-tubes, flasks, beakers, or dishes.

The two operations described in §§ 5 and 6, respectively, viz., FILTRATION and DECANTATION, serve to effect the mechanical separation of fluids from matter suspended therein.

§ 5.

4. FILTRATION.

This operation consists simply in passing the fluid, from which we wish to remove the solid particles mechanically suspended therein, through a filtering apparatus formed

usually by a properly arranged piece of unsized paper placed in a glass funnel. An apparatus of this description allows the fluid to trickle through, while it retains the solid particles. We employ *smooth filters* and *plaited filters;* the former in cases where the separated solid substance is to be made use of, and the latter where the object is simply to clear the solution rapidly. Smooth filters, which are placed in the funnel in such a manner that they are everywhere in contact with it, are obtained by folding a circular paper twice so that the folds are at right angles. The preparation of plaited filters, which may be accomplished in various ways, is better shown than described.

In cases where the contents of the filter require washing, the paper must not project over the rim of the funnel. In most cases, it is advisable to moisten the filter previously to passing the fluid through it, since this not only tends to accelerate the process, but also renders the solid particles less liable to be carried through the pores of the filter. The paper selected for filters must be as free as possible from inorganic substances, especially such as are dissolved by acids, *e.g.*, calcium and iron compounds.

FIG. 1.

The common filtering-paper of commerce seldom comes up to our needs in this respect, and I would therefore recommend always washing it carefully with dilute hydrochloric acid whenever it is intended for use in *accurate analyses*. For this purpose, the apparatus shown in Fig. 1 will be found convenient. *A* is a bottle with the bottom taken out; *a* and *b* are glass plates, and between them lie the filters, which have been previously cut

and folded; *d* is a glass tube fitted into the cork *c*; *e* is a piece of flexible tube, which is closed by a piece of glass rod or a clip. The bottle is filled with a mixture of one part hydrochloric acid, sp. gr. 1.12, and two parts water, in which the filters are allowed to soak from 4 to 8 hours, the acid being then run off and replaced by ordinary water. After an hour, this is replaced by fresh water, and so on till the washings are barely acid. The washing is continued with distilled water till the washings are free from hydrochloric acid, that is, till they cease to give any turbidity when mixed with a few drops of solution of silver nitrate. Finally, the filters are drained, turned out upon blotting-paper, covered with the same, and dried in a sieve in a warm place. When we merely wish to wash two or three filters, we place them in a funnel as in filtering, one inside the other, moisten them with dilute hydrochloric or nitric acid, and after some time wash them well with distilled water.

Filtering-paper, to be considered good, must, besides being pure, also let fluids pass readily through, while completely retaining even the finest pulverulent precipitates, such as barium sulphate, calcium oxalate, etc. If a paper satisfying these requirements cannot be readily procured, it is advisable to keep two sorts, one of greater density for the separation of very finely divided precipitates, and one of greater porosity for the speedy separation of grosser particles. For the past few years, cut filters of all sizes, both washed and unwashed, have been manufactured on a large scale and can be purchased. Quite recently, filters hardened by treatment with nitric acid have been sold, and these are characterized by increased filtering capacity as well as by being but little attacked by acids and alkalies.

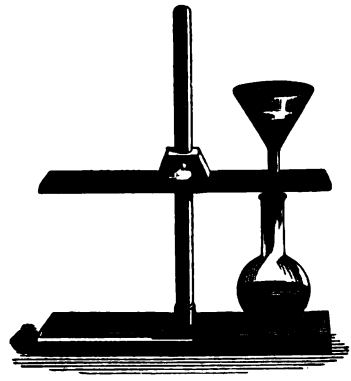

FIG. 2.

The funnels must be of glass (§ 19, 9). It is best to place them upon a stand to insure a firm position. For

smaller filtrations, such as are customary in qualitative analysis, a stand of the form shown in Fig. 2 is to be recommended.

§ 6.

5. Decantation.

This operation is frequently resorted to instead of filtration in cases where the solid particles to be removed are of considerably greater specific gravity than the liquid in which they are suspended, as they will in such cases speedily subside to the bottom, thereby rendering it easy either to decant the supernatant fluid by simply inclining the vessel, or to draw it off by means of a siphon or a pipette.

Certain slimy or gelatinous precipitates so clog the pores of paper as scarcely to admit of filtration. To obtain the liquid in which they have been formed quite clear, decantation is indispensable. Oftentimes the two processes may be advantageously combined by allowing the precipitate to settle as much as possible, and then pouring off the still turbid liquid upon a filter.

§ 7.

6. Washing.

When filtration or decantation has been resorted to for the purpose of collecting a solid substance, the latter has to be freed afterward from the adhering liquid by repeated *washing* or *edulcoration*. The washing of precipitates collected on a filter is usually effected by means of a washing-bottle, such as is shown in Fig. 3.

This consists of a flask or bottle, closed with a twice-perforated, snugly-fitting rubber stopper, through which pass two glass tubes, as in the figure. The outer end of the tube *a* is drawn to a moderately fine point. If it is wished to have this movable, the tube *a* is cut in two between the point and the bend, and the two parts are united by means of a piece of rubber tubing. By blowing into the other tube, a stream of water is driven out from *a* with considerable force, which

adapts the apparatus to removing precipitates from the sides of vessels as well as to washing them on filters. This form of washing-bottle serves for washing with warm or even boiling water, provided the vessel itself has a uniformly thin bottom, so that it can be heated without fear of breaking. By binding about the neck a ring of cork, winding it closely with smooth cord, or providing it with a handle (Fig. 4), it may be held with convenience when its contents are hot. Washing by

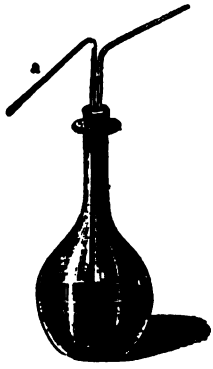

Fig. 3.

Fig. 4.

decantation is carried out, after pouring off the liquid, by simply stirring up the precipitate with water or any other liquid used for washing, allowing it to settle again, and decanting anew.

As the success of an analysis often depends upon the complete or proper washing of a precipitate, the operator must accustom himself to continue the process patiently until he is certain that the object in view has been actually accomplished. In general, this is not the case until the precipitate has been perfectly freed from the liquor in which it was formed. The analyst must not be content with *guessing* that a precipitate is thoroughly washed, but must *prove* that it is so by applying appropriate tests. If the body to be removed is non-volatile, slow evaporation of a few drops of the last portions of the washings on a clean surface of platinum will usually serve to indicate the point at which the process may terminate.

§ 8.

7. Dialysis.

Dialysis is an operation which may be employed for the separation of certain dissolved bodies from others. When superficially considered, it appears to possess a certain similarity to filtration, but in reality it differs essentially from that operation. It was introduced into science by Graham (Annal. der Chem. u. Pharm., **121**, 1), and depends upon the different behavior of bodies dissolved in water towards moist membranes. Bodies that are able to crystallize (crystalloids, Graham) have the power of penetrating certain membranes with which their solution may be placed in contact, while amorphous bodies, or colloids, viz., gum, gelatin, dextrin, caramel, tannic acid, albumen, silicic acid, etc., do not possess that property. Hence, the two classes may be separated by taking advantage of this action. The septum must consist of a colloid material, as the skin of an animal or, best of all, parchment-paper, and it must be in contact with water on the outer side. Figs. 5 and 6 exhibit suitable forms of apparatus for this operation. In Fig. 5, the dialyzer consists of the upper part of a bottle, closed at the base with parchment-paper; in Fig. 6, it consists of a hoop of wood or gutta-percha, covered below, like a sieve, with parchment-paper.

Fig. 5.

The disk of parchment-paper should measure about 10 cm more in diameter than the space to be covered. It should be moistened, stretched over, and fastened by a string or by an elastic band, but should not be secured too firmly. The parchment-paper must not be porous, and its soundness may be tested by sponging the upper side with water and observing whether wet spots show on the other side. Defects may be remedied by applying liquid albumen,

and coagulating this by heat. When the dialyzer has thus been put in perfect condition, the mass to be examined is poured into it. If the substance is entirely liquid, the

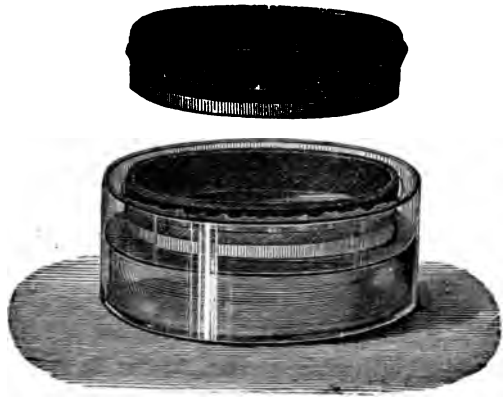

FIG. 6.

bell-shaped dialyzer may be chosen, but if it contains undissolved solid matter, the hoop is preferable. The depth of fluid in the dialyzer should not be more than 1.5 cm, and the membrane should dip a little below the surface of the water in the outer vessel, which should amount to at least four times the quantity of the fluid to be dialyzed. The bell-shaped dialyzer should be hung in the manner shown in Fig. 5, while the hoop may be allowed to float. After twenty-four hours, half or three fourths of the crystalloids will be found in the external water, while the colloids remain in the dialyzer; at most, only traces pass into the external fluid. If the dialyzer is brought successively in contact with fresh supplies of water, the whole of the crystalloids may be finally separated from the colloids. This operation is sometimes of service in chemico-legal investigations, for the extraction of poisonous crystalloids from parts of a dead body, or from food, vomit, etc.

There are four operations which serve to separate volatile substances from less volatile or from fixed bodies, viz., EVAPORATION, DISTILLATION, IGNITION, and SUBLIMATION. The first two relate to liquids, the others to solids.

§ 9.

8. Evaporation.

This operation is one of those most frequently used. It serves to separate volatile fluids from less volatile or from fixed bodies (solid or fluid) in cases where the residuary substance alone is of importance. Thus, we have recourse to evaporation for the purpose of removing from a saline solution part of the water, in order to bring about crystallization of the salt; also, for removing the whole of the water from the solution of a non-crystallizable substance, so as to obtain the latter in a solid form. The evaporated water is disregarded in these cases, the only object being to obtain in the one case a more concentrated fluid, and in the other a dry substance. These objects are attained by converting to the gaseous state the fluid which is to be removed. This is generally done by the application of heat; sometimes by leaving the fluid for a time in contact with the atmosphere or with an enclosed volume of air kept dry by hygroscopic substances, such as concentrated sulphuric acid, calcium chloride, etc.; or lastly, by placing the fluid in rarefied air, with simultaneous application of hygroscopic substances.

As it is of the utmost importance in qualitative analyses to guard against the least contamination, and as an evaporating fluid is the more liable to this the longer the operation lasts, the process is usually conducted, with proper expedition, in porcelain or platinum dishes, over the flame of a spirit- or gas-lamp, in a place free from dust, preferably in a cupboard or hood provided with a draught. If the operator has no place of this kind, he must have recourse to the inconvenient alternative of covering the dish. The best way of doing this is to place over it a large glass funnel, secured by a retort-holder, in such a manner as to leave sufficient space between the rim of the funnel and the border of the dish. The funnel should be placed slightly aslant, so that the drops running down its sides may be received in a beaker. This end is more fully attained by Victor Meyer's protection funnel.*

* Zeitschr. f. analyt. Chem., 23, 529.

This has its upper edge bent inward, forming a trough in which the condensed liquid collects, and flows through a tubulure which is attached to one side. The dish may also be covered with a sheet of filter-paper previously freed from inorganic substances by washing with dilute hydrochloric or nitric acid. Were common and unwashed filter-paper used for the purpose, the ferric oxide, lime, etc., contained in it would dissolve in the vapors evolved (more especially if acid), and the solution dripping down into the evaporating fluid would speedily contaminate it. Such precautions are necessary, of course, only in accurate analyses. Large quantities of fluid are sometimes evaporated best in flasks standing aslant over a charcoal fire or gas flame, or in tubulated retorts with the neck rising obliquely upward and with open tubulure. Evaporating processes at 100°are conducted in a suitable steam apparatus or on the water-bath shown in Fig. 7, upon which copper or porcelain rings may be placed, so that it can accommodate smaller dishes. Evaporation to dryness is not usually conducted over the naked flame, but generally either on the water-bath or the sand-bath, or on an asbestus or iron plate. It should be remembered that porcelain and glass vessels—which we can hardly avoid using for the evaporation of large quantities of fluids—are always somewhat acted upon, so that their contents become more or less contaminated. The action is but slight in case of most dilute acids or acid liquids, but the student should never evaporate *alkaline fluids* in glass, as, at a boiling temperature, they attack it considerably.

FIG. 7.

§ 10.

9. DISTILLATION.

This operation serves to separate a volatile liquid from a less volatile or a non-volatile substance, where the object is to recover the evaporating fluid. A distilling apparatus consists of three parts: 1st, a vessel in which the liquid to be distilled is heated, and thus converted into vapor; 2d, an apparatus in which this vapor is cooled again or condensed and thus recon-

verted to the fluid state; and 3d, a vessel to receive the fluid thus reproduced by the condensation of the vapor (the distillate). For the distillation of large quantities, metallic apparatus are used (copper stills with head and condenser of tin), or large glass retorts; in analytical investigations, we use either small retorts with receivers, or more usually an apparatus like that shown in Fig. 8. The fluid to be distilled is boiled in *A*, and the vapor escapes through the tube which is fitted into the cork. The tube is surrounded with a wider

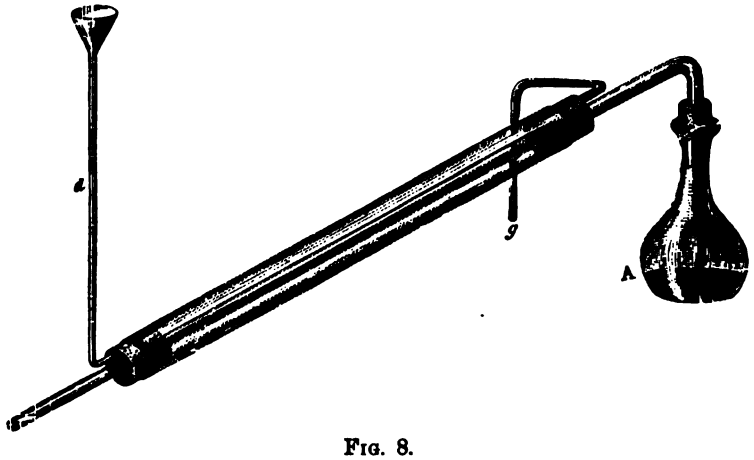

FIG. 8.

tube, which is filled with cold water, and this is renewed continually or occasionally by pouring in fresh water through *d*, after placing a vessel under *g* to catch the hot water which runs out. A small flask serves as a receiver.

§ 11.

10. IGNITION.

Ignition is, in a certain sense, for solid bodies what evaporation is to fluids, since it serves (at least generally) to separate volatile substances from less volatile or from fixed bodies, in cases where the residuary substance alone is of importance. Ignition always involves the use of a high temperature, and is thus distinguished from drying. The state which the volatilized body assumes upon cooling—whether it

remains in the gaseous state, as when calcium carbonate is ignited; whether it is liquid, as when calcium hydroxide is heated; or solid, as in the ignition of a mixture containing ammonium chloride—is quite immaterial as far as the name of the operation is concerned.

The object of ignition already mentioned is the common one, but in some instances, substances are ignited simply for the purpose of modifying their state, without any volatilization taking place, for example, in the conversion of the more bulky, more easily soluble form of alumina into the denser form which is more difficultly soluble in sulphuric acid. Substances are often ignited, also, in order that the operator may from their deportment at a red heat draw conclusions as to their nature in general, their fixity, their fusibility, the presence or absence of organic matter, etc.

Crucibles are the vessels generally made use of in ignition. In operations on a large scale, Hessian or graphite crucibles are used, heated by charcoal or gas; in analytical experiments, small-sized crucibles or dishes of porcelain, platinum, silver, or iron, or glass tubes sealed at one end, are selected, according to the nature of the substances to be ignited. These crucibles, dishes, or tubes are heated over a spirit- or gas-lamp, or a blast-lamp.

§ 12.

11. Sublimation.

The term *sublimation* designates the process which serves to convert solid bodies into vapor by the application of heat, and subsequently to recondense the vapor to the solid state by refrigeration. The substance thus volatilized and recondensed is called a *sublimate*. Sublimation is consequently a *distillation of solid bodies*. We have recourse to this process mostly in order to effect the separation of substances possessed of different degrees of volatility. It is of great importance in analysis for the recognition of several substances, for example, arsenic. The vessels used for sublimation are of variable sizes, according to the volatility of the substance. In sublimations for analytical purposes, we generally employ

closed glass tubes. When the sublimation is performed with the aid of a current of hydrogen or carbon dioxide, we use open glass tubes, which are usually made narrower just in front of the part to which the heat is applied. The substance may be placed directly in the tube, or it may be contained in a boat of platinum or porcelain.

§ 13.

12. Fusion and Fluxing.

Simple fusion is the conversion of a solid substance into the fluid form by the application of heat. It is most frequently resorted to for the purpose of effecting the combination or the decomposition of bodies. The term is also applied in cases where substances insoluble or difficult of solution in water and acids are by fusion, in conjunction with some other body, modified, decomposed, or fluxed in such a manner that they or the newly formed compounds will subsequently dissolve in water or acids. Fusion is conducted either in porcelain, silver, or platinum crucibles. The crucible is supported on a triangle of moderately stout platinum wire (with silver crucibles, iron wire), resting on, or attached to, the iron ring of the spirit- or gas-lamp. Pipe-stem triangles are also used. Small quantities of matter are often fused in glass tubes closed at one end.

Resort to fusion is especially required for the analysis of various insoluble sulphates, silicates, and aluminum compounds. The flux most commonly used is sodium carbonate, or potassium carbonate, or, better still, a mixture of *both* in molecular proportions. In certain cases, barium hydroxide is employed. For the fusion of aluminates, sodium or potassium disulphate is frequently used. A platinum crucible should be used for fusions with alkali carbonates, barium hydroxide, and alkali disulphates.

Precautionary rules for the prevention of damage to platinum vessels.—No substance evolving chlorine ought to be treated in platinum vessels. No sodium or potassium nitrate or hydroxide or cyanide, no metals or sulphides of metals, should be fused in such vessels; nor should readily deoxidizable metallic

oxides, or organic salts of the heavy metals, or phosphates in presence of organic compounds, be ignited in them. It is also detrimental to platinum crucibles to expose them directly to an intense charcoal fire, as this is likely to render them brittle. It is always advisable to support these vessels, when used in ignition or fusion, on triangles of platinum wire or of pipe-stem. When a platinum crucible has been made white hot over the bellows blowpipe, it is unwise to cool it too quickly by suddenly turning off the gas, and allowing the cold blast to play upon it, since, under these circumstances, the crucible is very liable to become slightly cracked.

Platinum crucibles which have become stained can be cleaned by rubbing with moist sea-sand, the grains of which are rounded and not inclined to scratch. If the stains or impurities in a platinum dish resist this treatment, acid potassium sulphate or borax should be heated in it to fusion for some time. The vessel is then cleaned with hot water, and finally, if needful, is burnished with sand as above described.

The following operation should also be described as one which is related to fusion:

§ 14.

13. Deflagration.

We understand by the term *deflagration*, in a more general sense, every process of decomposition attended with noise or detonation. We use the same term, however, in a more restricted sense, to designate the oxidation of a substance in the dry way, at the expense of the oxygen of another substance mixed with it (usually a nitrate or a chlorate), and connect with it the idea of sudden combustion attended with incandescence and detonation.

Deflagration is resorted to either to produce a desired body, or it is applied as a means to prove the presence or absence of a certain substance. Thus, arsenious sulphide is deflagrated with potassium nitrate to obtain potassium arsenate; and salts are tested for nitric or chloric acid by fusing

them with potassium cyanide, and observing whether they deflagrate, etc. To attain the former object, the perfectly dry mixture of the substance and the deflagrating agent is projected in small portions at a time into a red-hot crucible. Experiments of the latter description are invariably made with minute quantities, preferably on a piece of thin iron or platinum foil, or in a small spoon.

§ 15.

14. The Use of the Blowpipe.

This operation is of paramount importance in many analytical processes. We must examine here the apparatus required, the mode of its application, and the results of the operation.

The blowpipe, Fig. 9, is a small instrument, usually made of brass or German silver. It consists of three parts, viz., 1st, a tube, *ab*, fitted, for greater convenience, with a horn or ivory mouthpiece, through which air is blown from the mouth; 2d, a small cylindrical vessel, *cd*, into which *ab* is screwed air-tight, and which serves as an air-chamber, and to retain the moisture of the air blown into the tube; and 3d, a smaller tube, *fg*, also fitted into *cd*. This small tube, which forms a right angle with the larger one, is fitted at its aperture either with a finely perforated platinum plate, or more conveniently with a finely perforated platinum cap, *h*. The construction of the cap is shown in Fig. 10. This is a little more expensive than a simple plate, but it is also much more durable. If the opening of the cap becomes stopped up, the obstruction may generally be removed by heating it to redness before the blowpipe.

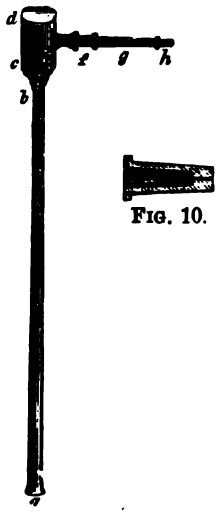

Fig. 9.

Fig. 10.

The proper length of the blowpipe depends upon the distance at which the operator can see with distinctness. It is

usually from 20 to 25 cm long. The form of the mouthpiece varies. Some chemists like it of a shape which may be encircled by the lips; others prefer a trumpet mouthpiece, which is only pressed against the lips. The latter requires less exertion on the part of the operator, and is accordingly generally chosen by those who do a great deal of blowpipe work.

The blowpipe serves to conduct a continuous fine current of air into a gas flame, or into the flame of a candle or lamp, or sometimes into an alcohol flame. The flame of a candle or lamp, burning under ordinary circumstances, consists of three principal parts, as shown in Fig. 11, viz., 1st, a dark nucleus, *a'a*, in the centre; 2d, a luminous cone, *efg*, surrounding this nucleus; and 3d, a feebly luminous mantle, *bcd*, encircling the whole flame. The dark nucleus contains the gases which the heat evolves from the wax or fat, and which cannot burn for want of oxygen. In the luminous cone, these gases come in contact with a certain amount of air insufficient for their complete combustion. In this part, therefore, it is principally the hydrogen of the hydrocarbons evolved which burns, while the carbon separates in a state of intense ignition, which imparts to the flame the luminous appearance observed in the cone. In the outer coat, the access of air is no longer limited, and all the matter not yet burned is consumed. This part of the flame is the hottest, and the extreme apex is its hottest point. Oxidizable bodies oxidize, therefore, with rapidity when placed in it, since all the conditions of oxidation (high temperature and an unlimited supply of oxygen) are here united. This outer part of the flame is therefore called the *oxidizing flame*. On the other hand, oxides having a tendency to yield up their oxygen suffer *reduction* when placed within the luminous part of the flame, the oxygen being withdrawn from them by the carbon and the still unconsumed hydrocarbons there present. The luminous part of the flame is therefore called the *reducing flame*.

FIG. 11.

The effect of blowing a fine stream of air across a flame is, first, to alter the shape of the flame, since, from tending up-

ward, it is now driven sideways in the direction of the blast, being at the same time lengthened and narrowed; and, in the second place, to extend the sphere of combustion from the outer to the inner part. As the latter circumstance causes an extraordinary increase in the heat of the flame, and the former, a concentration of that heat within narrower limits, it is easy to understand the exceedingly energetic action of the blowpipe flame. The way of holding the blowpipe and the nature of the blast will depend upon whether the operator needs a reducing or an oxidizing flame. The easiest way of producing most efficient flames of both kinds is by means of coal-gas delivered from a jet, shaped as in Fig. 18, the slit being 1 cm long and 1½ to 2 mm wide, as, with the use of gas, the operator is enabled to regulate not only the current of air, but that of the gas also. The task of keeping the blowpipe steadily in the proper position may be greatly facilitated by firmly resting that instrument upon some movable metallic support, such as the ring of BUNSEN'S gas-lamp intended for holding dishes, etc. Fig. 12 shows the flame for reducing; Fig. 13, the flame for oxidizing. The

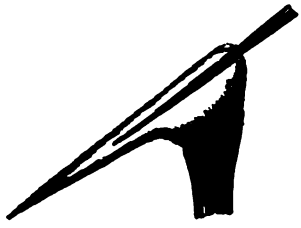

FIG. 12.

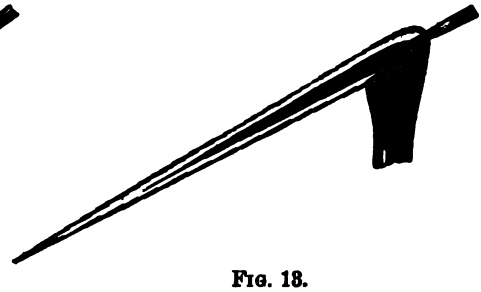

FIG. 13.

reducing flame is produced by keeping the jet of the blowpipe just on the border of a tolerably strong gas-flame, and driving a moderate blast across it. The resulting mixture of the air with the gas is only imperfect, and there remains between the inner bluish part of the flame and the outer barely visible part a luminous and reducing zone, of which the hottest point lies somewhat beyond the apex of the inner cone. To produce the *oxidizing flame*, the gas is lowered, the jet of the blowpipe pushed a little farther into the flame, and the strength of the current somewhat increased. This

serves to effect an intimate mixture of the air and gas, and an inner, pointed, bluish cone, slightly luminous towards the apex, is formed, and surrounded by a thin, pointed, light-bluish, barely visible mantle. The hottest part of the flame is at the apex of the inner cone. Difficultly fusible bodies are exposed to this part to effect their fusion, but bodies to be oxidized are held a little beyond the apex, that there may be no want of air for their combustion. An oil-lamp with a broad wick of proper thickness may be used instead of gas; a thick wax-candle also will do. For an oxidizing flame, a small spirit-lamp will in most cases answer the purpose.

The *current* is produced with the cheek muscles alone, and not with the lungs. The way of doing this may be easily acquired by breathing quietly, with distended cheeks and with the blowpipe between the lips. Practice and patience will soon enable the student to produce an even and uninterrupted current.

The *supports* on which substances are exposed to the blowpipe flame are generally either wood charcoal, or platinum wire or foil.

Charcoal supports are used principally in the reduction of metallic oxides, etc., or in testing the fusibility of bodies. The substances to be operated upon are put into small cavities, scooped out with a penknife or with a little tin tube. Metals that are volatile at the heat of the reducing flame evaporate wholly or in part upon the reduction of their oxides. In passing through the outer flame, the metallic vapors are re-oxidized, and the oxide formed is deposited upon the support around the heated substance. Such deposits are called coatings or incrustations. Many of these exhibit characteristic colors, leading to the detection of the metals. The charcoal of pine, linden, or willow, is greatly preferable to that of harder woods. Saw the thoroughly burnt charcoal of well-seasoned and straight-split pine into rectangular pieces, and brush off the dust. The blocks may then be handled without soiling the hands. The sides alone are used on which the annual rings are visible on the edge, as, on the other sides, the fused matters are apt to spread over the surface of the charcoal. Small supports are sometimes sold, which have been made

from powdered charcoal and pressed into convenient shapes. These are very serviceable and clean.

Charcoal is a valuable material for supports in blowpipe experiments because of—1st, its infusibility; 2d, its low conducting power for heat, which permits substances to be heated more strongly upon a charcoal than upon any other support; 3d, its porosity, which causes it to readily imbibe fusible substances, such as borax, sodium carbonate, etc., while infusible bodies remain on the surface; 4th, its reducing power, which greatly contributes to the reduction of oxides in the inner blowpipe flame.

We use *platinum wire*, and occasionally also *platinum foil*, in all oxidizing processes before the blowpipe; also when fusing substances with fluxes, to test their solubility, to watch the phenomena attending the solution, and to mark the color of the bead; and lastly, to introduce substances into the flame, to see whether they will color it. The wire should be cut into lengths of 8 cm, and each length bent at both ends

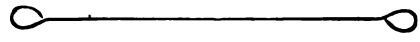

Fig. 14.

into a small loop (Fig. 14). When required for use, the loop is moistened with a drop of water, then dipped into the powdered flux (where a flux is used), and the portion adhering fused in the flame of a gas- or spirit-lamp. When the bead produced, which sticks to the loop, is cold, it is moistened again, and a small portion of the substance to be examined put on and made to adhere to it by the action of gentle heat. The loop is then finally exposed, according to circumstances, to the inner or the outer blowpipe flame.

What renders the application of the blowpipe particularly useful is the great expedition with which results are attained. These results are of a twofold kind, viz., they either afford us simply an insight into the general properties of the body, and accordingly enable us only to determine whether it is fixed, volatile, fusible, etc.; or the phenomena which we observe render us able to recognize at once the particular body which we have before us. We shall have occasion to describe

these phenomena when treating of the deportment of the different substances with reagents.

In using the blowpipe, one hand is always occupied; continuous blowing requires practice and some effort, although the latter may not be very great, and it is not very easy to maintain a blowpipe flame in such a manner that the substance exposed to it is always exactly in the desired part of the flame. For these reasons, the efforts of many chemists have been directed towards producing automatic blowpipes, and many such pieces of apparatus have been recommended and used. In some of these, the air-current is produced by means of a gasometer, in others by means of a rubber balloon, in others still by a species of hydrostatic blast, etc. The simplest self-acting apparatus, however, by which most of the objects attainable with the blowpipe may be conveniently accomplished, is a BUNSEN gas-lamp, which burns without luminosity and without soot. A description of this lamp is given in the next paragraph.

§ 16.

15. THE USE OF LAMPS, PARTICULARLY OF GAS-LAMPS.

As we have to deal mostly with small quantities of matter, we commonly use in processes of qualitative analysis requiring the application of heat, such as evaporation, ignition, etc., either spirit-lamps or gas-lamps.

Of *spirit-lamps*, there are two kinds in use, viz., the simple kind shown in Fig. 17, and the BERZELIUS lamp with double draught given in Fig. 15. In the construction of the latter, it should be borne in mind that the part containing the wick and the vessel holding the spirit must be in separate pieces, connected only by means of a narrow tube; otherwise, troublesome explosions are apt to occur in lighting the lamp. The chimney should not be too narrow, or the stopper fit too tightly on the mouth through which the spirit is introduced. A lamp should be selected that will readily slide up and down the pillar of the stand, which must be fitted with a movable brass ring to support dishes and flasks in processes

of ebullition, and a ring of moderately stout iron wire to support the triangle for holding the crucibles in the processes of ignition and fusion. Of the various forms of lamps in use, the one shown in Fig. 15 is the most suitable. Fig. 16 represents a triangle of platinum wire fixed within an iron-wire

FIG 15.

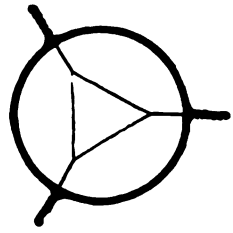

FIG. 16.

FIG. 17.

ring. This serves to support crucibles in processes of ignition. Glass vessels, more particularly beakers, which it is intended to heat over the lamp, are most conveniently rested on a piece of gauze made of brass wire such as is used in making sieves of medium fineness.

Of the many *gas-lamps* proposed, BUNSEN'S, as shown in its simplest form in Figs. 18 and 19, is the most convenient. *ab* is a base of cast iron. In the center of this is fixed a brass box, *cd*, which has a cylindrical cavity 12 mm deep and 10 mm in diameter. In each side of the box, 4 mm from the upper rim, is a circular aperture of 8 mm diameter, leading to the inner cavity. Fitted into one side, 1 mm below the circular aperture, is a brass tube, which serves for the attachment of the India-rubber supply-tube. This brass tube is made in the shape shown in Fig. 18, and has a bore of 4 mm. The gas conveyed into it passes into a tube in the center of the cavity of the box. The latter tube, which is 4 mm thick at the top and thicker at the lower end, projects 3 mm above the rim of the box. The gas issues from a narrow

opening which appears to be formed of 3 radii of a circle, inclined to each other at an angle of 120°. The length of each radius is 1 mm, and the opening of the slit is $\frac{1}{8}$ mm wide. *ef* is a brass tube 95 mm long, open at both ends, with a bore of 9 mm, and the screw at the lower end of this tube fits into

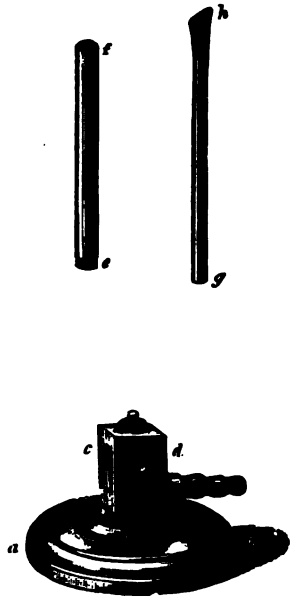

Fig. 18.

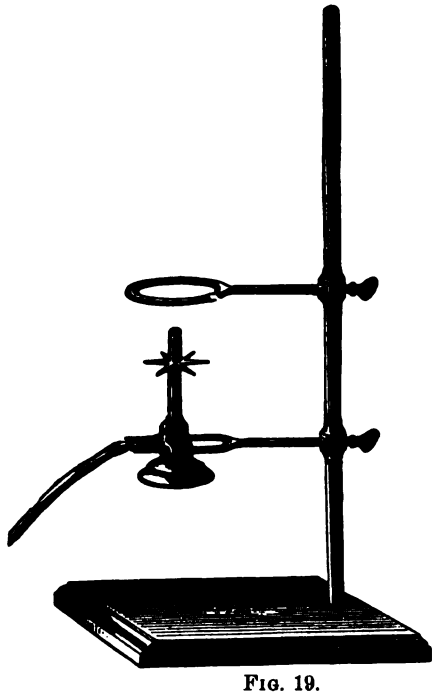

Fig. 19.

the upper part of the cavity of the box. With this tube screwed in, the lamp is completed. On opening the stop-cock, the gas rushes into the tube *ef*, where it mixes with the air coming in through the circular apertures. When this mixture is kindled at *f*, it burns with a straight, upright, bluish flame, entirely free from soot, which may be regulated at will by means of the stop-cock. A partial opening of the cock suffices to give a flame fully answering the purpose of the common spirit-lamp; while with the full stream of gas turned on, the flame, which will now rise up to 2 dm in height, affords a most excellent substitute for the Berzelius lamp. If the flame is made to burn very low, it will often occur that it recedes; in other words, instead of the

mixture of gas and air burning at the mouth of the tube *ef*, the gas takes fire on issuing from the slit, and burns below in the tube. This defect may be remedied by arranging the lamp so that not only the stream of gas, but also the air which enters, may be regulated, as in the lamp shown in Fig. 22; and also in the above described simple lamp, by covering the tube *ef* at the top with a little wire-gauze cap. Flasks, beakers, etc., which it is intended to heat over the gas-lamp, are supported upon brass or iron gauze, thin iron plates, or asbestus board. For blowpipe operations, the tube *gh* must be inserted into *ef*. This tube terminates in a flattened top, cut off at an angle of 68° to the axis, and having an opening 1 cm long and 1½ to 2 mm wide. The insertion of *gh* into *ef* serves to close the air-holes in the box, and pure gas, burning with a luminous flame, issues from the top of the tube. Fig. 19 shows the apparatus complete, fixed in the fork of an iron stand. This arrangement permits the lamp to be moved backward and forward between the prongs of the fork, and up and down the pillar of the stand. The movable ring on the same pillar serves to support the objects to be operated upon. The 6 radii around the tube of the lamp serve to support a sheet-iron chimney (see Fig. 23), or a porcelain plate used in quantitative analyses.

Fig. 20.

To heat crucibles to the brightest red heat or to a white heat, the *bellows blowpipe* is resorted to. But even without this, the action of the gas-lamp may be considerably heightened by heating the crucible within a small clay furnace, as recommended by Erdmann. Fig. 20 shows the simple contrivance by which this is effected. The furnaces are 115 mm high, and measure 70 mm in diameter in the clear. The thickness of material is 8 mm. If the ordinary Bunsen burner is not sufficiently strong for any purpose, the three-Bunsen burner (Fig. 21) may be used. A similar purpose is served by the very effective gas-furnaces of W. Hempel * and H. Roessler.†

* Zeitschr. f. analyt. Chem., 16, 454 and 18, 404. † *Ibid.*, 25, 95 and 32, Heft 5.

BUNSEN has devised a more perfect form of this lamp* to render the flame a more complete substitute for the blowpipe flame, namely, for reducing, oxidizing, fusing, and volatilizing, and for the observation of the coloration of flame (§ 17). This improved form is shown in Fig. 22. *a* is a sheath, which can be turned around for regulating the flow of air. When in use, a conical chimney (*ddd'd'*, Fig. 23) is

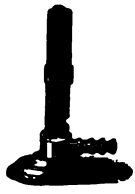

FIG. 21.

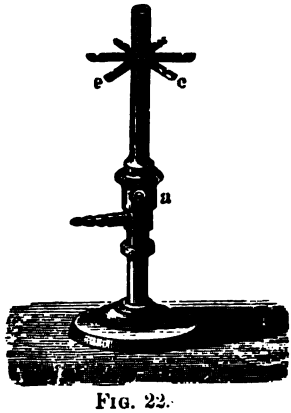

FIG. 22.

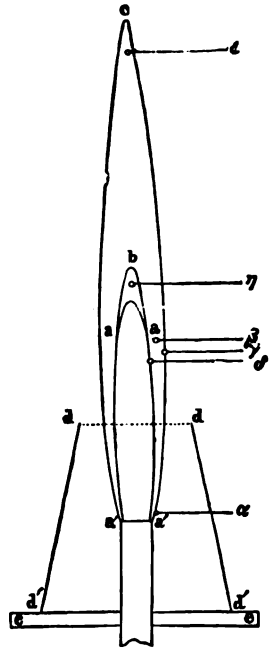

FIG. 23.

placed on *ee*, and is of such dimensions that the flame will burn tranquilly. Fig. 23 shows the flame half its natural size. In this, three parts are at once apparent, namely, (1) the dark cone, *aaa'a'*, which contains the cold gas mixed with about 62 per cent of air; (2) the mantle, *a'ca'b*, formed by the burning mixture of gas and air; (3) the luminous tip of the dark cone, *aba*, which does not appear unless the air-holes are somewhat closed. The last is useful for reductions.

Such are the three principal parts of the flame, but

* Annal. d. Chem. u. Pharm., 111, 257, and 138, 257. Also, Zeitschr. f. analyt. Chem., 5, 351.

BUNSEN distinguishes no less than six parts, which he names as follows:

1. *The base* at α, which has a relatively low temperature, because the burning gas is here cooled by the constant current of fresh air, and also because the lamp itself conducts the heat away. This part of the flame serves for discovering the colors produced by readily volatile bodies when less volatile bodies which color the flame are also present. At the relatively low temperature of this part of the flame, the former volatilize alone instantaneously, and the resulting color imparted to the flame is for a moment visible, unmixed with other colors.

2. *The fusing zone.* This lies at β, at a distance of somewhat more than one third of the height of the flame from the bottom, and equidistant from the outside and the inside of the mantle, which is broadest at this part. This is the hottest part in the flame (about 2300° BUNSEN), and it therefore serves for testing substances as to their fusibility, volatility, emission of light, and for all processes of fusion at a high temperature.

3. *The lower oxidizing flame* lies in the outer border of the fusing zone at γ, and is especially suitable for the oxidation of oxides dissolved in vitreous fluxes.

4. *The upper oxidizing zone* at ϵ consists of the non-luminous tip of the flame. Its action is strongest when the air-holes of the lamp are fully open. It is used for the roasting away of volatile products of oxidation, and generally for all processes of oxidation where the very highest temperature is not required.

5. *The lower reducing zone* lies at δ, in the inner border of the fusing zone next to the dark cone. The reducing gases are here mixed with oxygen, and therefore do not possess their full power. Hence, they are without action on many substances which are deoxidized in the upper reducing flame. This part of the flame is especially suited for reduction on the charcoal stick (p. 34), or in vitreous fluxes.

6. *The upper reducing flame* lies at η, in the luminous tip of the dark inner cone, which, as I have already explained, may be produced by diminishing the supply of air. This part of the flame must not be allowed to get large enough to blacken a test-tube filled with water and held in it. It contains no

free oxygen, is rich in separated incandescent carbon, and therefore has a much stronger action than the lower reducing zone. It is used more particularly for the reduction of metals collected in the form of incrustations.

With the help of a gas flame of this description, we can obtain as high a temperature as with the blowpipe, and even higher if the radiating surface of the substance is made as small as possible. Moreover, by the use of the different parts of the flame, processes of reduction and of oxidation may be carried out with the greatest convenience.

In order to study *the deportment of bodies at a high temperature*, namely, their emission of light, fusibility, volatility, and power of coloring flame, they are introduced into the flame in the loop of a platinum wire, which should be barely thicker than a horse-hair. Should the substance attack platinum, a little bundle of asbestus is used, which should be about one fourth the thickness of a match. Decrepitating substances are first very finely powdered, then placed on a strip of moistened filter-paper about a square centimeter in surface, and this is cautiously burnt between two rings of fine platinum wire. The substance now presents the appearance of a coherent crust, and may be held in the flame without difficulty. For testing fluids to see whether they contain a substance which colors flame, the round loop of the fine platinum wire is flattened on an anvil to the form of a small ring. This is dipped into the fluid, and then withdrawn, when a drop will be found attached to the ring. This drop is held near the flame and allowed to evaporate without boiling, after which the residue may be conveniently tested.

If bodies are to be exposed to the action of the flame for a considerable time, the stand shown in Fig. 24 is used. *A* and *B* are provided with springs, and can be easily turned and moved up and down. On *A* is the arm *a*, intended for the support of the platinum wire fixed in the glass tube (Fig. 25); also another little arrangement to hold the glass tube *b*, with its bundle of asbestus fibers, *d*. *B* bears a clip for the reception of a test-tube, which in certain cases has to be heated for a considerable time in a definite part of the flame. *C* serves to hold the various platinum wires fixed in glass tubes.

Experiments of reduction are performed either with the aid

of a suitable reducing agent in a small glass tube, or with the aid of a little stick of charcoal. In order to prepare the latter, BUNSEN recommends holding an uneffloresced crystal of sodium carbonate near the flame, and, after having taken off the head of a match, smearing three fourths of its length with the wet mass produced by warming the crystal. The match-stick is then slowly rotated on its axis in the flame, when a crust of solid sodium carbonate will form on the carbonized wood, and on heating in the fusing zone of the flame, this crust will be melted and absorbed by the charcoal. The little stick of charcoal will now be protected in a measure from combustion. The substance to be tested is made into a paste, with a drop of melted crystallized sodium carbonate, and a mass about the size of a millet-seed is taken up on the point of the carbonized match. It is then first melted in the lower oxidizing flame, and afterwards moved through a portion of the dark cone into the opposite hottest part of the lower reducing zone. The reduction will be rendered evident by the effervescence of the sodium carbonate. After a few moments, the action is stopped by allowing the substance to cool in the dark cone of the flame. If, finally, the point of the carbonized match is cut off and triturated with a few drops of water in a small agate mortar, the reduced metal will be obtained in the form of sparkling fragments, which may be purified by elutriation, and, if necessary, more minutely examined.

FIG. 25.

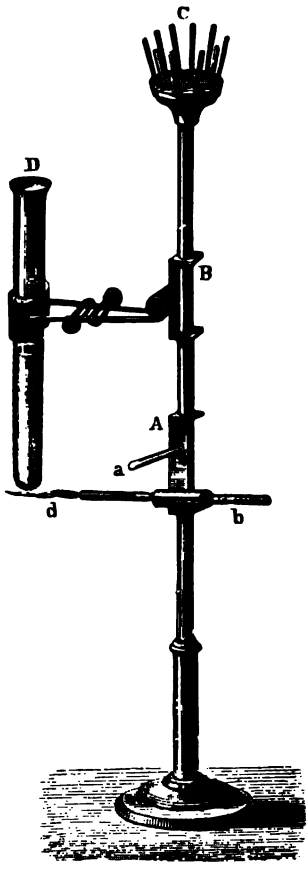

FIG. 24.

Volatile elements which are reducible by hydrogen and carbon may be separated as such or as oxides from their combinations, and deposited on porcelain. These deposits are called *incrustations*. They are thicker in the middle, and become thin towards the edges. They may be converted into iodides, sulphides, and other combinations, and thus may be further identified. These reactions are so delicate that in many cases a quantity of from $\frac{1}{10}$ to 1 mg is sufficient to exhibit them.

The metallic incrustation is obtained by holding in one hand a small portion of the substance on asbestus, in the upper reducing flame; and in the other a glazed porcelain dish, from 1 to 1.2 dm in diameter, filled with water, close over the asbestus, in the upper reducing flame. The metals separate as sooty or mirror-like incrustations.

If the substance is held as just directed, and the porcelain dish is held in the upper oxidizing flame, an *incrustation of oxide* is obtained. In order to be sure of getting it, the flame must be comparatively small if the portion of substance is minute. To turn the incrustation of oxide into an *incrustation of iodide*, let the dish covered with the oxide cool, breathe on it, and place it on a wide-mouthed bottle (Fig. 26). This bottle contains phosphorus tri-iodide, which has been allowed to deliquesce and become converted into fuming hydriodic acid and phosphorous acid. It should have an air-tight glass stopper. If the hydriodic acid has become so moist that it has ceased to fume, it may be restored to its proper condition by the addition of phosphorus pentoxide. To turn the incrustation of iodide into an *incrustation of sulphide*, direct a current of air containing ammonium sulphide upon it, breathing upon the dish occasionally; then drive off the excess of ammonium sulphide by *gentle* warming.

FIG. 26.

If more considerable quantities of the metallic incrustation are required for further experiments, the porcelain dish is replaced by a test-tube (*D*, Fig. 24) half filled with water, in which a few pieces of marble should be placed to prevent bumping when the water boils. In this case, the asbestus (*d*, Fig. 24), with the substance on it, is fixed at the same

height as the middle of the upper reducing flame; the test-tube is fixed with its bottom close over the asbestus, as shown in the figure, and the lamp then is moved just under the test-tube. The substance thus comes within the reducing flame, and the metallic incrustation forms on the bottom of the test-tube. The incrustation may be obtained as thick as is wished by renewal of the substance.

§ 17.

16. Observation of the Coloration of Flame and Spectrum Analysis.

Many substances give characteristic tints to a colorless flame, which afford excellent means for their identification. For instance, salts of sodium impart to flame a yellow, salts of potassium a violet, salts of lithium a carmine tint, and thus may be easily distinguished from each other.

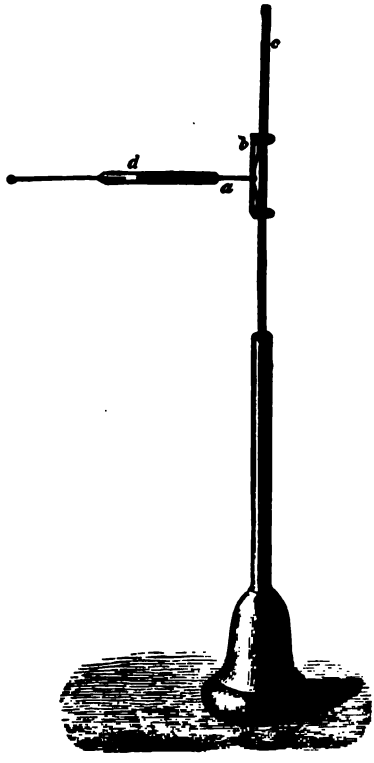

Fig. 27.

The flame of Bunsen's gas-lamp with chimney, described in § 16 and shown in Fig. 22, is more particularly suited for observations of this kind. The substances to be examined are put on the small loop of a fine platinum wire, and by means of the holder shown in Fig. 24, or the more simple one, Fig. 27, then placed in the fusing zone of the gas flame. A particularly striking coloration is imparted to the flame by the volatile salts of the alkali and alkali-earth metals. If different salts of one and the same base are compared in this way, it is found that each one of them, if

at all volatile at high temperatures, or permitting at least the volatilization of the base, imparts the same color to the flame, but with different degrees of intensity, the most volatile of the salts producing also the most intense coloration. For instance, potassium chloride gives a more intense coloration than potassium carbonate, and the latter again a more intense one than potassium silicate. In the case of difficultly volatile compounds, the coloration of the flame may often be developed by adding some other body which has the power of decomposing the compound under examination. Thus, in silicates containing only a few per cent of potassium, the latter body cannot be directly detected by coloration of flame. This detection may be accomplished, however, by adding a little pure gypsum, as this will cause formation of calcium silicate and potassium sulphate, a salt which is sufficiently volatile.

For continuous observation of the colorations which the chlorides of the heavy metals impart to the flame, MITSCHERLICH'S method can be used. This consists in passing a stream of hydrogen through a bulb-tube, in the bulb of which the metallic chloride is heated; and the hydrogen issuing from the end of the tube, which is bent upward and drawn out, is ignited. The following apparatus (Fig. 28), described by VOGEL, and arranged for the use of illuminating-gas, can also be used for this purpose. The gas is led in through *k*, passes through *s*, and then burns at the top of the BUNSEN burner of glass, which is held by the wire *u*. If the burner is rightly constructed and adjusted, the flame will be non-luminous. If the substance at *p* is now heated, the flame will show quickly and continuously the coloration corresponding to the intermixed chloride.

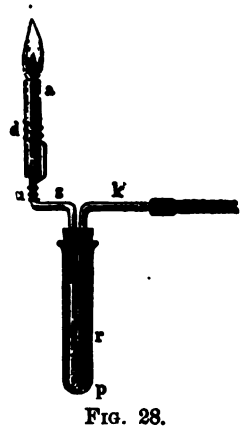

FIG. 28.

But however decisive a test the mere coloration of flame affords for the detection of certain metallic compounds, when present unmixed with others, this method becomes apparently useless in the case of mixtures of compounds of several

metals. For instance, mixtures of salts of potassium and sodium show only the sodium flame; mixtures of salts of barium and strontium, only the barium flame, etc. This defect may be remedied, however, in two ways.

The *first way*, introduced by CARTMELL,* and afterwards perfected by BUNSEN† and by MERZ,‡ consists in looking at the colored flame through some colored medium (colored glasses, indigo solution, etc.). Such media, in effacing the flame coloration of one metal, bring out that of the other mixed with it. For instance, if a mixture of a salt of potassium and a salt of sodium is exposed to the flame, the latter will show only the yellow sodium coloration; but if the flame be now looked at through a deep-blue cobalt glass, or through a solution of indigo, the yellow sodium coloration will disappear and be replaced by the violet potassium tint. A simple apparatus suffices for every observation and experiment of this kind, all that is required for the purpose being—

1. A hollow prism (Fig. 29) composed of mirror-plates, the chief section of which forms a triangle with two sides of 150 mm and one side of 35 mm length. The indigo solution required to fill this prism is prepared by dissolving 1 part of indigo in 8 parts of fuming sulphuric acid, adding to

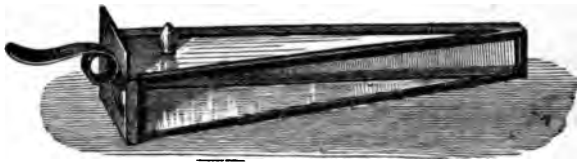

FIG. 29.

the solution 1500–2000 parts of water, and filtering. When using this apparatus, the prism is moved in a horizontal direction close before the eye, in such a way that the rays of the flame are made to penetrate successively thicker and thicker layers of the effacing medium. CORNWALL§ prefers a solution of potassium permanganate to the indigo, since it

* Phil. Mag., **16**, 328. † Annal. d. Chem. u. Pharm., **111**, 257.
‡ Journ. f. prakt. Chem., **80**, 487.
§ American Chemist, **2**, 384; Zeitschr. f. analyt. Chem., **11**, 307.

allows the distinct recognition of the potassium flame in the presence of compounds of sodium, lithium, and calcium. He gives to the sides of the hollow prism a length of 240 mm, and to the thick end an interior diameter of 30 mm, and uses a solution of potassium permanganate of such strength that, at a distance of 45 mm from the thick end, the strongest sodium or lithium flame is completely effaced.

2. A blue, a violet, a red, and a green glass. The blue glass is tinted with cobalt oxide; the violet glass, with manganese sesquioxide; the red glass (white glass colored red superficially), with cuprous oxide; and the green glass, with iron oxide and cupric oxide. The colored glass of commerce will generally be found to answer the purpose. In regard to the tints imparted to the flame by the different bodies when viewed through the aforesaid media, and the combinations by which these bodies are severally identified, information will be found in Section III, in the paragraphs treating of the several metals and acids.

The *second way*, which is called *Spectrum Analysis*, was introduced by KIRCHHOFF and BUNSEN. It consists in letting the rays of the colored flame first pass through a narrow slit, then through a prism, and observing the rays so refracted through a telescope. A distinct spectrum is thus obtained for every flame-coloring metal. This spectrum consists either of a number of colored lines lying side by side, as in the case of barium; or of two, separate, differently colored lines, as in the case of lithium; or of a single green line, as in the case of thallium. These spectra are characteristic in a double sense, *i.e.*, the spectrum lines have a distinct color, and they also occupy a fixed position.

It is this latter circumstance which, in the spectrum observation of mixtures of flame-coloring metals, enables us to identify without difficulty every individual metal. Thus, a flame in which a mixture of potassium, sodium, and lithium salts is evaporated, will give, side by side, the spectra of the several metals in the most perfect purity.

KIRCHHOFF and BUNSEN have constructed two forms of apparatus which are adapted for spectroscopic observation, and by which measurements of the positions in which the spectral lines appear may be made. Both depend upon exactly the

same principles. The larger and more complete apparatus is described and figured in POGGENDORFF'S Annalen, **113**, 374, and in the Zeitschr. f. analyt. Chem., **1**, 49. The smaller, simpler, and consequently cheaper apparatus, which suffices for ordinary purposes, and is used very frequently in laboratories, will be described here. It is shown in Fig. 30.

A is an iron disk, in the center of which a prism, with cir-

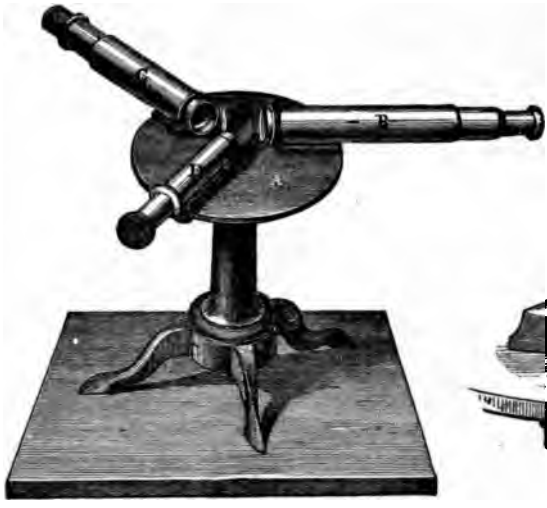

FIG. 30.

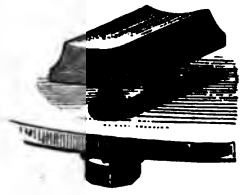

FIG. 30*a*.

cular refracting faces of about 25 mm diameter, is fastened by a clamp and screw. The same disk has also attached to it the three tubes *B*, *C*, and *D*. Each of these tubes is soldered to a metal block (Fig. 30*a*), by which they may be adjusted in the proper position. *B* is the observation telescope. It has a magnifying power of about six, and an objective of about 20 mm diameter. The tube *C* is closed at one end by a brass disk, into which is cut the perpendicular slit through which the light is admitted. The tube *D* carries a photographic copy of a millimeter scale, on a glass plate reduced to about one fifteenth the original dimensions. This scale is covered with tin-foil, with the exception of the narrow strip upon which the divisional lines and the numbers are engraved. It is lighted by a gas or candle flame placed before it.

The axes of the tubes *B* and *D* are directed to the center of one face of the prism, at the same inclination, while the

axis of the tube *C* is directed to the center of the other face. This arrangement makes the spectra produced by the light passing through *C*, and the image of the scale in *D*, produced by total reflection, appear in one and the same spot, so that the positions occupied by the spectrum lines may be read off on the scale. The prism is placed in about the position in which there is a minimum divergence of the rays of the sodium line, and the telescope is set in the direction in which the red and the violet potassium lines are about equidistant from the middle of the field of view.

The colorless flame into which the flame-coloring bodies are to be introduced is placed 10 cm from the slit. BUNSEN'S lamp, shown in Fig. 22, gives the best flame. The lamp is adjusted so as to place the upper border of the chimney about 20 mm below the lower end of the slit. When this lamp has been lighted, and a bead of substance—say, of potassium sulphate—introduced into the fusing zone by means of the holder shown in Fig. 27, the iron disk of the spectrum apparatus, which, with all it carries, is movable round its vertical axis, is turned until the point is reached where the luminosity of the spectrum is the most intense.

To cut off foreign light in all spectrum observations, the central part of the apparatus is covered with a black cloth or box.

If reflected sunlight is allowed to pass through the slit of the spectroscope, a continuous spectrum showing the rainbow colors is obtained, in which a number of dark lines can be detected. (Compare 1 in the table of spectra.) These dark, FRAUNHOFER'S lines assume fixed places in the spectrum, and therefore serve as definite starting-points for determining the positions of other lines. They are due to the fact that the rays emanating from the solid or fluid body of the sun pass through the sun's atmosphere. The gaseous bodies of which this is formed, which would give bright spectrum lines of their own accord, absorb out of the white sunlight, exactly those parts which they themselves radiate, and thus cause the dark lines.

If reflected sunlight (or also lamplight) which enters the slit passes through liquids, it either goes through these unabsorbed, or is partly absorbed. In the latter case, dark

stripes or bands are observed in the spectrum, which, since they are caused by the extinction of rays of certain refrangibility, assume definite positions in the spectrum, and they may serve, therefore, for the characterization of many substances. For the observation of such *absorption-spectra*, the liquids to be examined are placed in vessels of colorless glass, best in such as have straight, parallel walls.

Besides the spectroscope of BUNSEN and KIRCHHOFF, many other forms have come into use,* among which I will call special attention to the universal spectroscopes of H. W. VOGEL † and C. H. WOLFF, ‡ which are also convenient for the observation of flame-spectra and absorption-spectra.

The spectra yielded by the alkalies and alkali-earths, and also those of thallium and indium, are portrayed in Table I. The spectra are represented as they appear in instruments provided with astronomical telescopes. In Section III, attention will be called to the lines which are most characteristic for each metal. In this place, I will merely show the manner in which the greatest certainty may be attained in spectrum analysis. This is done by placing beads of pure metallic compounds in the flame, and registering the most prominent spectral lines upon a drawn scale, in the position which they show upon the scale of the instrument. For the sake of an example, this has been done for strontium upon the upper scale in the spectral table. It is evident that the spectrum of an unknown body can only pass as a strontium spectrum when the characteristic lines correspond not only in regard to their color, but also to the exact positions in which they have been drawn upon the strontium scale.

Such drawings, as is evident, must be prepared by each operator for his own apparatus, and they lose their significance if anything is changed in the arrangement of the prism or scale. On this account, it is advisable to give a setting to the apparatus which can easily be found again if it should be disturbed by accident; for example, one in which the left-hand edge of the sodium line corresponds to division 50.

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* Compare Zeitschr. f. analyt. Chem., **2**, 64, 190, and 353; **3**, 443; **5**, 329; **12**, 432; **13**, 48, and 442; **14**. 335; **16**. 463; **17**, 187; **19**, 72; **20**, 99; **21**, 182, 241, and 554; **22**. 540; **25**, 379; **26**, 124, and 616; **28**, 330; **30**. 816, and 467; **31**, 63.

† *Ibid.*, **17**, 187.

‡ *Ibid.*, **20**, 99.

In regard to the observation of *spark-spectra*, I refer to the article of R. BUNSEN, which treats this subject fully (Zeitschr. f. analyt. Chem., **15**, 68).

With the appearance of spectrum analysis, an era which is new in many respects has begun in chemical analysis, for we are able by this means to discover much smaller amounts of substances than is possible with any other method. At the same time, the process gives a certainty which satisfies every doubt, and yields results in seconds which formerly, if attainable at all, were only to be obtained in hours or days.

§ 18.

17. THE USE OF THE MICROSCOPE IN QUALITATIVE ANALYSIS.

It has already been pointed out in § 3 that the microscope is used for the observation of very small crystals. While this instrument was formerly used only exceptionally, it has gained much significance recently through the investigations of O. LEHMANN,* K. HAUSHOFER,† A. STRENG,‡ H. BEHRENS, § FREY, ‖ and others. These researches have demonstrated that not only occasional substances, but numerous bodies, can be detected by the help of microscopic analysis, and in many cases even when they are accompanied by other substances.

The foundation of this method of investigation is the fact that bodies which have a tendency to crystallize show the same crystalline form under identical conditions of formation. Now, since these forms are different with different bodies, and in many cases are characteristic for special ones, the microscopic observation of the crystals often allows the accurate recognition of elements or of certain of their compounds.

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* Annal. d. Physik u. Chem. [N. F.], 13, 506. Zeitschr. f. analyt. Chem., 21, 92.

† "Mikroskopische Reactionen" v. K. HAUSHOFER, Braunschweig, 1885.

‡ Ber. d. oberhessischen Gesellsch. f. Natur- u. Heilkunde, 22, 258 *et seq.* Zeitschr. f. analyt. Chem., 23, 185.

§ Ann. de l'École polyt. de Delft, 1891. Zeitschr. f. analyt. Chem., 30, 125 *et seq.*

‖ Schweitz, Wochenschr. f. Pharm., 30, 149. Zeitschr. f. analyt. Chem., 32, 204.

As far as the carrying out of work in microscopic analysis is concerned, it generally deals with the formation of crystals which are produced upon the object-glass, either by mixing a drop of the liquid to be investigated with a drop of an appropriate precipitating agent, or by the careful evaporation of a drop of a certain solution of the substance to be recognized. The resulting crystals are usually observed when magnified from 50 to 200 times, sometimes with the help of NICOL'S prisms.

It follows from what has been said that only very small amounts of substances are necessary for the performance of such microscopic analyses, and that the object is attained in a relatively short time. In many cases, reliable results are obtained without difficulty, but in others, the task is rendered difficult by the circumstance that, with small changes in the conditions of formation, regularly formed crystals are often not obtained, but instead crystal skeletons or aggregations, including many crystals which are mostly incompletely developed.

The advantages which microscopic analysis offers are consequently obvious, and although this method can scarcely replace the usual methods of chemical analysis, yet it often supplements them in a very efficient manner.

However, if reliable results are to be obtained by its use, microscopic analysis requires not only a thorough knowledge of crystallography, but also extensive practice in the use of the microscope. Therefore, those who are taking up analytical chemistry cannot readily learn the former subject, in its fullest extent, simultaneously with purely chemical methods. It should rather be made an object of special study. In the present work, I shall limit myself by mentioning only the microscopic reactions which have special value for detecting certain bodies, and shall refer, for the rest, to the treatises which have been cited above. In HAUSHOFER'S work, the descriptions of the microscopic appearance of crystals are supplemented by illustrations.

APPENDIX TO SECTION I.

§ 19.

Apparatus and Utensils.

Since it might be difficult for many who are beginning the pursuit of chemical analysis to distinguish the most suitable from the unnecessary things, in their choice of the apparatus and utensils required for the purpose, I here add a list which contains the apparatus really necessary for carrying out simple investigations. I also take this opportunity to call attention to some points which are to be kept in view in buying or preparing them.

1. A Bunsen burner with chimney, and inner tube for producing a flame for blowpiping, together with a lamp-stand (§ 16, Figs. 18, 19, and 22).

If illuminating-gas is not available, Berzelius's alcohol-lamp (§ 16, Fig. 15) and a glass alcohol-lamp (§ 16, Fig. 17) can be used.*

2. A blowpipe (see § 15).

3. A platinum crucible of about 15 cc capacity, the cover of which is in the form of a shallow dish, and which is not too deep in proportion to its width.

4. Platinum foil, as smooth and clean as possible, and not too thin; length about 40 mm; width about 25 mm.

5. Platinum wire (see pp. 26 and 34). Two larger and two finer wires are amply sufficient to begin with. They are kept most conveniently in a glass half filled with dilute acid; the wires may thus be kept clean.

6. A stand with twelve or more test-tubes. 16 to 18 cm is the proper length of the tubes; from 1 to 2 cm the proper width. The tubes must be made of thin white glass, and well annealed. The rim must be quite round, slightly flared,

* [The dealers supply certain forms of gasoline-lamps, which give a non-luminous flame similar to that of the Bunsen gas-burner, and even superior to it in heating power. These are recommended as being far cheaper in regard to fuel, more convenient, and more powerful than alcohol-lamps.]

and without a lip, since this is of no use for pouring, and it interferes greatly with corking the tubes, as well as with thorough shaking. The stand shown in Fig. 31 will be found convenient. The pegs upon the upper shelf are for hold-

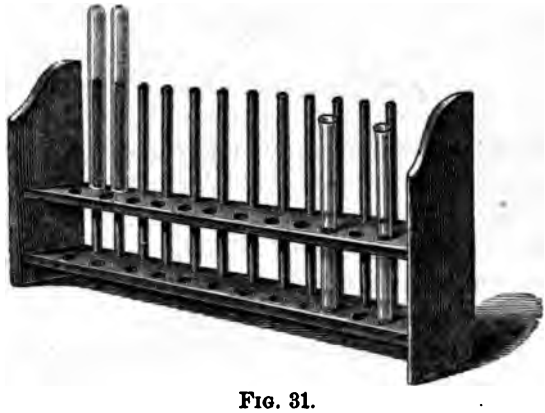

FIG. 31.

ing the test-tubes after they are washed. In this position, they can drain well, and are always clean and dry.

7. SEVERAL NESTS OF BEAKERS AND SOME SMALL FLASKS of thin, well-annealed glass.

8. SEVERAL PORCELAIN EVAPORATING-DISHES,* AND VARIOUS SMALL PORCELAIN CRUCIBLES. Those of the royal manufacture of BERLIN are unexceptionable both in shape and durability. Those of MEISSEN and NYMPHENBURG are also very good.

9. SEVERAL GLASS FUNNELS of various sizes. These must be inclined at an angle of 60°, and merge into the neck at a definite angle.

10. A WASHING-BOTTLE of a capacity of from 300 to 400 cc (see § 7).

11. AN ASSORTMENT OF GLASS TUBES, SOME GLASS RODS, AND A GLASS SPATULA. The former may be bent, drawn out, etc., over a BERZELIUS lamp or gas-lamp; the rods are rounded at the ends by fusion.

12. A selection of WATCH-GLASSES.

*[Porcelain dishes with handles, called CASSEROLES, are very convenient for evaporation in qualitative analysis. These can be held by hand over the naked gas flame, and the operator, besides securing very rapid evaporation, is enabled to stop the process at the proper point. The size most useful for the purpose is 3A of the royal Berlin make.]

13. A small AGATE MORTAR.

14. STEEL OR BRASS PINCERS, 10 or 12 cm long.

15. A WOODEN FILTER-STAND (see § 5).

16. A TRIPOD of thin iron, to support the dishes, etc., which are to be heated over the small spirit- or gas-lamp.

17. WIRE GAUZES OR ASBESTUS BOARDS (§ 16).

18. A PLATINUM TRIANGLE or an iron triangle supplied with pipe-stems (§ 16, Fig. 16).

19. Pieces of COLORED GLASS, especially blue and green (§ 17).

20. A PIPETTE holding 10 cc, graduated in half cubic centimeters.

21. FILTER-PAPER, or ready-made filters.

SECTION II.

REAGENTS.

§ 20.

A VARIETY of phenomena may manifest themselves upon the decomposition or combination of bodies. In some cases, liquids change their color; in others, precipitates are formed; sometimes effervescence takes place, and sometimes deflagration, etc. Now, if these phenomena are very striking, and attend only upon the action of two definite bodies upon one another, it is obvious that the presence of one of these bodies may be detected by means of the other. If we know, for instance, that a white precipitate of certain definite properties is formed upon mixing baryta with sulphuric acid, it is clear that, if upon adding baryta to any liquid we obtain a precipitate exhibiting these properties, we may conclude that this liquid contains sulphuric acid.

Those substances which indicate the presence of others by any striking phenomena are called *reagents*.

According to the different objects attained by the application of these bodies, we make a distinction between *general* and *special reagents*. By *general reagents* are meant those which serve to determine the class or group to which a substance belongs; and by *special reagents*, those which serve to detect bodies individually. That the line between the two divisions cannot be drawn with any degree of precision, and that one and the same substance is often made to serve both as a general and a special reagent, cannot well be held as valid objections to this classification, which is simply intended to induce a habit of employing reagents always for a settled purpose, viz., either simply to find out the *group* to which the substance belongs, or to determine the latter *individually*

While the usefulness of *general reagents* depends principally upon their efficiency in strictly characterizing groups of bodies, and often effecting a complete separation of the bodies belonging to one group from those belonging to another, that of *special reagents* depends upon their being characteristic and sensitive. We call a reagent *characteristic* if the alteration produced by it, in the event of the body tested for being present, is so distinctly marked as to admit of no mistake. Thus, iron is a characteristic reagent for copper, stannous chloride for mercury, because the phenomena produced by these reagents, —the separation of metallic copper and of globules of mercury—admit of no mistake. We call a reagent *sensitive* or *delicate* if its action is distinctly perceptible, even though only a very minute quantity of the substance tested for be present; for instance, starch as a reagent for iodine.

Very many reagents are both characteristic and delicate; for example, hydrochlorauric acid for stannous salts, potassium ferrocyanide for ferric and cupric salts, etc.

I hardly need mention that, as a general rule, reagents must be chemically pure, *i.e.*, they must consist purely and simply of their essential constituents, and must contain no admixture of foreign substances. We must therefore make it an invariable rule to *test the purity of reagents before we use them*, whether they be articles of our own production or purchased. Although the necessity of this is fully admitted, yet we find that in practice it is too often neglected. Thus, it is by no means uncommon to see aluminium entered among the substances detected in an analysis, simply because the solution of sodium hydroxide used as one of the reagents happened to contain that element; or iron, because the ammonium chloride used was not free from that metal. In this section, the directions given for testing the purity of the several reagents refer, of course, only to the presence of foreign matter resulting from the mode of their preparation, and not to mere accidental admixtures.

One of the most common sources of error in qualitative analysis proceeds from missing the proper measure—the right quantity—in the application of reagents. Such terms as *addition in excess*, *supersaturation*, etc., often induce novices to suppose that they cannot add *too much* of the reagent,

Consequently, some will *fill* a test-tube with acid simply to supersaturate a few drops of an alkaline fluid, whereas *every drop* of acid added after the neutralization point has been reached is to be looked upon as an excess of acid. On the other hand, the addition of an insufficient amount is to be equally avoided, since a reagent added in insufficient quantity often produces phenomena quite different from those which will appear if the same reagent be added in excess. For example, a solution of mercuric chloride yields a *white* precipitate if tested with a *small* quantity of hydrogen sulphide; but if treated with the same reagent *in excess*, the precipitate is *black*. Experience has proved, however, that the most common mistake beginners make is to add the reagents too copiously. One reason why this over-addition must impair the accuracy of the results is obvious: we need simply to bear in mind that the changes effected by reagents are perceptible within certain limits only, and, therefore, that they may be the more readily overlooked the nearer we approach these limits by diluting the fluid. Another reason lies in the fact that a *large excess* of a reagent will often have a solvent or modifying action upon a precipitate or color, and will entirely prevent the exhibition of phenomena which a suitable quantity would produce without difficulty.

No special and definite rules can be given for avoiding this source of error. However, a general rule may be laid down which will be found to answer the purpose, if not in all, at least in the great majority of cases. It is simply this: *Before the addition of a reagent, let the student always reflect for what purpose he applies it, what are the phenomena he intends to produce, and what are the results of the addition of excess.*

We divide reagents into two classes, according to whether the fluidity which is indispensable for their action upon the various bodies is brought about by the application of heat or by means of liquid solvents. We have, consequently, 1, *Reagents in the wet way;* and 2, *Reagents in the dry way.* For greater clearness, we subdivide these two principal classes as follows:

A. REAGENTS IN THE WET WAY.

I. Simple Solvents.

II. Acids and Halogens.

a. Oxygen acids.
b. Hydrogen acids and halogens.
c. Sulphur acids.

III. Bases, Metals, and Sulphides.

a. Oxygen bases and metals.
b. Sulphides.

IV. Peroxides.

V. Salts.

a. Of the alkali metals.
b. Of the alkali-earth metals.
c. Of the heavy metals.

VI. Coloring Matters and Indifferent Vegetable Substances.

B. REAGENTS IN THE DRY WAY.

I. Fluxes.

II. Blowpipe Reagents.

A. REAGENTS IN THE WET WAY.

I. Simple Solvents.

Simple solvents are fluids which do not enter into real chemical combination with the bodies dissolved in them. They will accordingly dissolve any quantity of matter up to a certain limit, which is called the point of saturation, and is dependent upon the temperature of the solvent. The essential and characteristic properties of the dissolved substances (taste, reaction, color, etc.) are not destroyed by the solvent (see § 2).

§ 21.

1. Water, H_2O.

Preparation.—Pure water is obtained by distilling well-water from a copper still, with head and condenser made of pure tin (not as well from a glass retort). The distillation is carried to about three fourths of the quantity operated upon. If it is desired to have the distilled water perfectly free from carbonic acid and ammonium carbonate, the portions passing over first must be rejected. In the larger chemical laboratories, distilled water is obtained from the steam apparatus which serves for drying, etc. In many cases, rain-water collected in the open air may be substituted for distilled water.*

Tests.—Water must be colorless, odorless, and tasteless. It should not change the color of test-papers, and should not leave the smallest residue when evaporated in a platinum vessel. It should not be changed by ammonium sulphide (copper, lead, iron), nor rendered turbid by baryta-water (carbonic acid). Even after long standing, no cloudiness should be caused by the addition of ammonium oxalate (lime), of barium chloride and hydrochloric acid (sulphuric acid), of silver nitrate and nitric acid (chlorides). Tested with potassium iodide, starch paste, and dilute sulphuric acid, there should be no blue coloration after standing a short time (nitrous acid), and it should not give a yellow color (ammonia) with an alkaline solution of potassium mercuric iodide (Nessler's reagent). A water which is free from reducing inorganic compounds may be tested for organic substances by coloring it very pale red with a trace of potassium permanganate, heating it to boiling, and observing if the reddish color remains, as is the case with pure water.

Uses.—We use water† as a simple solvent for a great variety of substances. A supply of it is kept in large glass flasks or in stoneware vessels. The most convenient way of using it is with the washing-bottle (see § 7, Fig. 3 or 4), by

* As regards the preparation of water absolutely free from organic matter, see Stas, Zeitschr. f. analyt. Chem., 6, 417.

† In analytical experiments we use only distilled water. Whenever, therefore, the term *water* occurs in the present work, distilled water is meant.

which means, a stronger or finer stream may be obtained. It also serves to precipitate substances which are insoluble in it from their solution in alcohol, strong acids, and other solvents, and also to effect the decomposition of several normal metallic salts (more particularly antimony trichloride and the salts of bismuth), in which case, the water combines with a part of the acid, while the remainder is contained in the basic salt which separates.

§ 22.

2. Ethyl Alcohol, C_2H_5OH.

Preparation.—For chemical analysis are needed, first, alcohol of .830 to .834 sp. gr. at 15.5°, corresponding to 91.17 to 90 per cent by volume (or the commercial "95 per cent" alcohol); and second, absolute alcohol. The latter is most conveniently prepared by digesting in a distilling flask, for two or three days, 1 part of fused calcium chloride with 2 parts of commercial spirit of about 96 per cent by volume, until solution has taken place, then distilling slowly and fractionating. As long as the distillate has a lower specific gravity than .8037 (corresponding to 98 per cent by volume), it may serve as absolute alcohol. The subsequent portions are collected separately.

Tests.—Alcohol must be colorless, and must completely volatilize when heated upon the water-bath. It ought not to leave a smell of fusel-oil when rubbed between the hands, nor should it alter the color of moist blue or red litmus-paper. When kindled, it must burn with a faint bluish, barely perceptible flame. To test it for traces of tar, it is mixed with 3 volumes of water, when, after the disappearance of air-bubbles, it must remain clear, not opalescent. Hydrogen sulphide water should give neither a coloration nor a precipitation.

Uses.—Alcohol serves (*a*) to effect the separation of bodies soluble in this fluid from others which do not dissolve in it, *e.g.*, of calcium nitrate from strontium nitrate; (*b*) to precipitate from aqueous solutions many substances which are insoluble in dilute alcohol, *e.g.*, gypsum, calcium malate;

(*c*) to produce various kinds of ether, *e.g.*, ethyl acetate, which is characterized by its peculiar and agreeable smell; (*d*) to reduce, usually with the co-operation of an acid, certain peroxides and metallic acids, *e.g.*, lead dioxide, chromic acid, etc.; (*e*) to detect certain substances which impart a characteristic tint to its flame, especially boric acid, strontium, potassium, sodium, and lithium.

§ 23.

3. Ethyl Ether, $(C_2H_5)_2O$.

4. Chloroform, $CHCl_3$.

5. Carbon Disulphide, CS_2.

Of these solvents, ether is the most frequently used. In the analysis of inorganic substances, it serves (mixed with absolute alcohol) for the separation of the nitrates of barium and strontium from calcium nitrate, for the recognition of chromic acid by means of hydrogen peroxide, for the detection and separation of bromine and iodine, for extracting ferric sulphocyanide from its aqueous solutions, etc. Ether is extensively used in the investigation of substances containing organic compounds, especially in searching for alkaloids in cases of poisoning. Chloroform is similarly used, but not so frequently. This serves, as does also carbon disulphide, especially for the detection and separation of bromine and iodine, and both these solvents are to be preferred to ether for this purpose.

These preparations are far more readily prepared on a large than on a small scale, and are consequently best obtained by purchase.

Tests.—Ether must be colorless, must have a specific gravity of .720 to .725 at 17.5°, and it should require about 12 parts of water for solution. The solution ought not to change the color of test-papers. Even at the common temperature, ether must rapidly and completely evaporate on a watch-glass, and it is especially important that it should leave no residue with an odor when thus treated. When shaken with a drop of bright mercury, it ought not to blacken

this, nor produce the separation of any black, pulverulent mercuric sulphide. If some solid potassium hydroxide is covered with ether in a test-tube and a little water is added, no brown color should appear, even after a long time. If ether is poured slowly, with cooling, into concentrated sulphuric acid, it ought to dissolve without coloration. If it is shaken with some potassium iodide solution containing a few drops of acetic acid, there should be no coloration produced, due to the separation of iodine. In keeping ether, it should be protected from the action of light.

Chloroform must be transparent and colorless and have a specific gravity of from 1.490 to 1.493 at 15°. Shaken with 2 volumes of water, its volume must not be perceptibly diminished, and the water should not assume an acid reaction nor should it be made turbid by the addition of silver nitrate solution. Even at the common temperature, chloroform must readily and completely evaporate on a watch-glass.

Carbon disulphide should be colorless, completely volatile at the common temperature, and exercise no action upon lead carbonate or upon moistened, blue litmus-paper.

II. Acids and Halogens.

§ 24.

The acids, at least those of pronounced character, are soluble in water. The solutions taste sour and redden litmus. Acids are divided into oxygen acids, hydrogen acids, and sulphur acids.

The oxygen acids (*anhydrides*), resulting generally from the combination of a non-metallic element with oxygen, combine with water in definite proportions—according to the views of dualistic chemistry—to form acid hydrates. It is with the latter that we have most to do. They are contained in the aqueous solutions of acid; they are usually designated by the names of the free acids, because the union of the water does not take away the acid properties. If they act upon metallic oxides, the oxide takes the place of the water of hydration, and an oxygen salt results: $H_2O.SO_3 + K_2O =$

$K_2O.SO_3 + H_2O$. If such salts arise from the combination of the acid with a strong base, the salts react neutral, provided that the acid, also, was a strong one. If, on the other hand, the base was a weaker one, for example, the oxide of a heavy metal, then the salts react acid. The latter are nevertheless called neutral (normal) salts, if the proportion of the oxygen of the base to the oxygen of the acid remains the same as is observed in the recognized neutral salts of the same acids, that is, if it corresponds to the saturating capacity of the acid. Sulphate of potash, $K_2O.SO_3$, reacts neutral; blue vitriol, $CuO.SO_3.5H_2O$, reacts acid. The latter, however, is called neutral (normal) sulphate of copper, because the oxygen of the copper oxide is to that of the sulphuric acid in the ratio 1 : 3, that is, in the same ratio in which the oxygen of the potash stands to that of the sulphuric acid in sulphate of potash, which is known to be neutral.

According to more recent chemical views, it is not the acid anhydrides that are called acids, but the compounds which are characterized in dualistic chemistry as acid hydrates, and the formation of salts takes place by the replacement of hydrogen atoms by metallic atoms: $H_2SO_4 + Zn = ZnSO_4 + H_2$.

The *hydrogen acids* arise from the combination of the halogens with hydrogen. Most of them show the character of acids in a pronounced degree. They neutralize oxygen bases, forming halogen salts and water: $2HCl + Na_2O = 2NaCl + H_2O$; $6HCl + Fe_2O_3 = Fe_2Cl_6 + 3H_2O$. The halogen salts which proceed from the action of strong hydrogen acids upon strong bases react neutral, while the solutions of those which are produced by the action of strong hydrogen acids upon weak bases (for example, alumina and ferric oxide) react acid.

The *sulphur acids* result more frequently from the combination of metallic than of non-metallic elements with sulphur. They combine—in the sense of dualistic chemistry—with sulphur bases to form sulphur salts: $As_2S_3 + 3Na_2S = 3Na_2S.As_2S_3$. The sulphur acids are therefore analogous to the oxygen acids, and from the standpoints of dualistic and modern chemistry, the ways of viewing them vary in the same way from each other as in the case of the oxygen acids dif-

cussed above. Since the sulphur acids are weak, all the sulphur salts which are soluble in water react alkaline.

a. Oxygen Acids.

§ 25.

1. Sulphuric Acid, H_2SO_4.

We use—

a. Concentrated sulphuric acid of commerce, so-called *oil of vitriol.* Colorless, sometimes also pale yellowish, oily liquid of 1.830 to 1.833 sp. gr.

b. Concentrated pure sulphuric acid.—Colorless, oily liquid of 1.836 to 1.840 sp. gr.

I will here state that pure sulphuric acid is now so easily obtained from factories where platinum apparatus is employed, that the chemist in the laboratory is seldom required to prepare it for himself. Moreover, the preparation from glass retorts is disagreeable, and not entirely free from danger. For the production of chemically pure sulphuric acid from the common acid, however, I recommend the following methods:

α. Put 1000 g of ordinary concentrated sulphuric acid in a porcelain dish, add 3 g of ammonium sulphate, and heat till copious fumes of sulphuric acid begin to escape, in order to destroy the oxides of nitrogen which are present. After cooling, add 4 or 5 g of coarsely powdered manganese dioxide, and heat to boiling, with stirring (Blondlot), in order to convert any arsenious acid into arsenic acid. When cool, pour off the clear fluid, by means of a long funnel-tube, into a retort coated with clay. The retort should not be more than half full, and is to be heated directly over charcoal. To prevent bumping, rest the retort on an inverted crucible cover, so that the sides may be more heated than the bottom. The neck of the retort must reach so far into the receiver that the acid distilling over drops directly into the body. To cool the receiver by means of water is unnecessary and even dangerous. To prevent the receiver coming into actual contact with the hot neck of the retort, some asbestus in large fibers is

placed between them. When about 10 or 15 g have been driven over, change the receiver, and slowly distil off three fourths of the contents of the retort. This method depends on the fact discovered by BUSSY and BUIGNET, that, on distilling sulphuric acid which contains arsenic in the form of arsenic acid, an arsenic-free distillate is obtained.

β. Pour into 4 parts of water 1 part of concentrated sulphuric acid, and conduct into the mixture for some time a slow stream of hydrogen sulphide, keeping the fluid heated to 70°. Let the mixture stand at rest for several days, then decant the clear supernatant fluid from the precipitate, which consists of sulphur, lead sulphide, perhaps also arsenic sulphide, and heat the decanted fluid in a tubulated retort, with upturned neck and open tubulure, until sulphuric acid fumes escape with the aqueous vapor. The acid so purified is fit for many purposes of chemical analysis. If it is wished, however, to free it from non-volatile substances also, it may be distilled from a coated retort as in *α*. As soon as the drops in the neck of the retort become oily, the receiver is changed, and the concentrated acid which then passes over is kept in a separate vessel.

c. Common dilute sulphuric acid.—To 5 parts of water in a lead or porcelain dish add gradually and while stirring, 1 part of the concentrated sulphuric acid.

Tests.—Pure sulphuric acid must be colorless. When a colorless solution of ferrous sulphate is poured upon it in a test-tube, no brown tint must mark the plane of contact of the two fluids (nitric acid, nitrous acid, nitrogen peroxide, perhaps also selenium). If the coloration is due to an oxygen compound of nitrogen, it will disappear by heating; if it is due to selenium or one of its acids, selenium separates as a red precipitate by heating. When diluted with 20 parts of water, it must not impart a blue tint to a solution of potassium iodide mixed with starch paste (nitrous acid, nitrogen peroxide). Mixed with pure zinc and water, it must yield hydrogen gas, which on being passed through a red-hot tube, must not deposit the slightest trace of arsenic. It must leave no residue upon evaporation on platinum, and must remain perfectly clear upon dilution with 4 or 5 parts of alcohol (lead, iron, calcium). The presence of small

quantities of lead is detected most easily by adding some hydrochloric acid to the sulphuric acid in a test-tube. If the plane of contact is marked by turbidity (lead chloride), lead is present. Sulphurous acid is discovered by the odor after shaking the acid in a half-filled bottle, or by finding if the acid diluted with water decolorizes water which is colored blue with iodized starch. The simplest way to test for ammonia is by means of NESSLER'S reagent (§ 96), after the acid has been largely diluted with water and the solution made somewhat alkaline with potassium hydroxide.

Uses.—Sulphuric acid has for most bases a greater affinity than almost any other acid. It is therefore used principally for the liberation and expulsion of other acids, especially phosphoric, boric, hydrochloric, nitric, and acetic acids. The great affinity of sulphuric acid for water is the cause of the decomposition of many bodies which cannot exist without water (*e.g.*, oxalic acid), when they are brought into contact with concentrated sulphuric acid. The nature of the decomposed body may in such cases be inferred from the products of decomposition. Sulphuric acid is also used for the evolution of certain gases, more particularly of hydrogen and hydrogen sulphide. It also serves as a special reagent for the detection and precipitation of barium, strontium, and lead.

The kind of sulphuric acid (whether pure or common commercial, whether concentrated or dilute) that should be used in each case is shown by a consideration of the circumstances, and, moreover, it will be generally stated in this book. In using common oil of vitriol, it should be borne in mind that where the sulphurous acid used for its manufacture is made from pyrites it may be very much contaminated with the acids of arsenic. Such arseniferous sulphuric acid cannot be used for finer analytical purposes, and it is not at all adapted for the evolution of hydrogen; for when the diluted acid acts upon zinc, hydrogen arsenide is given off with the hydrogen.

§ 26.

2. Nitric Acid, HNO_3.

Preparation.—a. Take crude nitric acid of commerce, as free as possible from chlorine, and of a specific gravity of at least 1.31 (a weaker acid will not answer the purpose), heat it to boiling in a glass retort, with addition of some potassium nitrate; let the distillate run into a receiver kept cool, and find from time to time whether, after dilution, it still continues to precipitate or cloud solution of silver nitrate. As soon as this ceases to be the case, change the receiver, and distil until a trifling quantity only remains in the retort. Dilute the distillate with water until the specific gravity is 1.2.

b. Dilute crude nitric acid of commerce, of about 1.38 sp. gr., with two fifths of its weight of water, and add solution of silver nitrate as long as a precipitate of silver chloride continues to form; then add a further slight excess of solution of silver nitrate, let the precipitate subside, decant the perfectly clear, supernatant acid into a retort or an alembic with a ground head; add some potassium nitrate free from chlorine, and distil until only a small quantity remains, taking care to attend to the proper cooling of the vapors distilling over. Dilute the distillate, if necessary, with water until it has a specific gravity of 1.2.

Tests.—Pure nitric acid must be colorless, and leave no residue upon evaporation on platinum foil. Solution of silver nitrate or of barium nitrate must not cause the slightest turbidity in it when diluted with at least 3 parts of water. To test more accurately for sulphuric acid and to test for iodic acid, a somewhat larger amount is evaporated in a porcelain dish over an alcohol-lamp (not a gas-lamp) to a small volume. This is taken up with water, and a portion of the solution is tested with barium nitrate. Some carbon disulphide is added to the remainder of the liquid, a very minute quantity of hydrogen sulphide water or aqueous solution of sulphurous acid is added, and, after shaking, any violet coloration of the carbon disulphide is observed. Lower oxides of nitrogen are recognized by the fact that the acid, diluted

with 5 parts of water, is instantly made blue by a solution of starch paste and potassium iodide. These lower oxides are removed by passing air or carbonic acid through the moderately warm acid. The presence of silver is detected by the addition of hydrochloric acid to the diluted acid, and the occasional presence of selenious acid is detected by evaporating off the nitric acid and heating the residue with hydrochloric and sulphurous acids.

Uses.—Nitric acid serves as a chemical solvent for metals, oxides, sulphides, oxygen salts, etc. With metals and sulphides of metals, the acid first oxidizes the metal present, at the expense of part of its own oxygen, and dissolves it as nitrate. Most oxides are dissolved by nitric acid at once as nitrates, and so are most of the insoluble salts with weaker acids, the latter being expelled in the process by the nitric acid. Nitric acid also dissolves salts with soluble non-volatile acids, as calcium phosphate, with which it forms calcium nitrate and acid calcium phosphate. Nitric acid is used also as an oxidizing agent, *e.g.*, to convert ferrous salts into ferric salts, stannous salts into stannic salts, etc.; also for the recognition of certain alkaloids which produce characteristic color-reactions with nitric acid.

§ 27.

3. Acetic Acid, $HC_2H_3O_2$.

Since a very concentrated acetic acid is never needed in qualitative analysis, the dilute acid of commerce suffices for the purpose. This is obtained, by the distillation of pure sodium acetate with sulphuric acid and some water, of 1.040 sp. gr., corresponding to a contents of 29 per cent acetic acid.

Tests.—Pure acetic acid must leave no residue upon evaporation, and, after saturation with sodium carbonate, emit no empyreumatic odor. Hydrogen sulphide, solution of silver nitrate, and solution of barium nitrate must not color or cloud the dilute acid, nor must ammonium sulphide after neutralization of the acid by ammonia. Solution of indigo

must not lose its color when heated with the acid. Empyreumatic matter is best detected by neutralizing the acid with sodium carbonate, and adding solution of potassium permanganate. If the acid is free from empyreumatic matter, no decolorization takes place in the course of ten minutes.

If the acid is not pure, add some sodium acetate and redistil from a glass retort, not quite to dryness. If it contains sulphur dioxide (in which case hydrogen sulphide will produce a white turbidity in it), digest it first with lead dioxide or finely pulverized manganese dioxide, and then distil, not fully to dryness, with sodium acetate.

Uses.—Acetic acid possesses a greater solvent power for some substances than for others. It is used, therefore, to distinguish the former from the latter. It thus serves to distinguish calcium oxalate from calcium phosphate. Acetic acid is used also to acidulate fluids where it is wished to avoid the employment of mineral acids.

§ 28.

4. Tartaric Acid, $H_2C_4H_4O_6$.

The tartaric acid of commerce may be sufficiently pure. It must dissolve clear in water, and the diluted solution should not be colored, made turbid, nor a precipitate be formed by the addition of hydrogen sulphide, barium chloride, calcium sulphate, or silver nitrate solutions. The solution, when made alkaline with ammonia, ought not to be colored or made turbid by either ammonium sulphide or ammonium oxalate. The tartaric acid should leave no residue when burnt in a platinum dish. It is kept in powder, as its solution suffers decomposition after a time, with the formation of mould. For use, it is dissolved in a little water with the aid of heat.

Uses.—The addition of tartaric acid to solutions of salts of various metals, especially of iron and aluminium, prevents the usual precipitation of these metals by an alkali. This non-precipitation is owing to the formation of double tar-

trates, which are not decomposed by alkalies. Tartaric acid may therefore be employed to effect the separation of these metals from other bodies, the precipitation of which it does not prevent. Tartaric acid forms a difficultly soluble salt with potassium, but not so with sodium. It is therefore one of our best reagents to distinguish between the two metals. *Acid sodium tartrate*, $HNaC_4H_4O_6$, answers the latter purpose still better than the free acid. This reagent is prepared by dissolving one of two equal portions of tartaric acid in water, neutralizing with sodium carbonate, then adding the other portion of the acid, and evaporating the solution to the crystallization point. For use, 1 part of the salt is dissolved in about 10 parts of water.

b. Hydrogen Acids and Halogens.

§ 29.

1. Hydrochloric Acid, HCl.

Preparation.—Pour a cooled mixture of 7 parts of concentrated sulphuric acid, which contains neither arsenic nor oxides of nitrogen (see § 25), and 2 parts of water over 4 parts of sodium chloride in a retort; expose the retort, with slightly raised neck, to the heat of a sand-bath until the evolution of gas ceases; conduct the evolved gas, by means of a bent tube, into a flask containing 6 parts of water, and take care to keep this vessel constantly cool. To prevent the gas from receding, the tube ought to dip but about 2 mm into the water of the flask. When the operation is terminated, try the specific gravity of the acid produced, and dilute with water until it marks from 1.11 to 1.12. Pure hydrochloric acid can also be prepared from the crude acid of commerce, which at present usually contains arsenic. For this purpose, a concentrated solution of stannous chloride is added to it in sufficient amount so that after twenty-four hours a portion of the acid will give a white precipitate with mercuric chloride—an indication that the stannous chloride is present in excess. The resulting brown precipitate, containing all the arsenic and some tin, is allowed to settle, and the acid is separated from

the precipitate by decantation or, if necessary, by filtration through asbestus. The acid is brought into a retort with the addition of from 1 to 5 per cent of sodium chloride, according to the amount of sulphuric acid that it contains; then placing 60 parts of water in the receiver for every 100 parts of concentrated acid, and without luting the receiver to the retort, it is distilled until nearly all the acid has gone over.

Tests.—Hydrochloric acid must be perfectly colorless and leave no residue upon evaporation. If it turns yellow on evaporation, ferric chloride is probably present, but organic substances may also give a similar color. It must not impart a blue tint to a solution of potassium iodide mixed with starch paste (chlorine or ferric chloride), must not destroy indigo-blue (chlorine), nor discolor a fluid made faintly blue with iodized starch (sulphur dioxide). Barium chloride ought not to produce a precipitate in the highly diluted acid (sulphuric acid). Small traces of sulphuric acid, however, cannot be discovered in this manner. If such are to be tested for, a considerable quantity of the hydrochloric acid should be evaporated on the water-bath over an alcohol-lamp (not a gas-lamp) to a very small residue, and this, after taking it up in water, should be tested with barium chloride solution. Hydrogen sulphide must leave the diluted acid unaltered (arsenious acid, possibly also selenious acid or stannic chloride). After neutralization with ammonia, ammonium sulphide must produce no change in it (iron, thallium). With zinc which is free from arsenic, it must evolve pure (arsenic-free) hydrogen.

Uses.—Hydrochloric acid serves as a solvent for many substances. It dissolves many metals and sulphides of metals as chlorides, with evolution of hydrogen or of hydrogen sulphide. It dissolves metallic oxides and peroxides in the form of chlorides, in the latter case usually with liberation of chlorine. Salts with insoluble or volatile acids are also converted by hydrochloric acid into chlorides, with separation of the original acid. Thus, calcium carbonate is converted into calcium chloride, with liberation of carbon dioxide. Hydrochloric acid dissolves salts with non-volatile and soluble acids apparently without decomposing them (*e.g.*, calcium phosphate); but the fact is that in cases of this kind

a metallic chloride and a soluble acid salt of the acid of the dissolved compound are formed. For instance, in the case of calcium phosphate, calcium chloride and acid calcium phosphate are formed. With salts of acids forming no soluble acid compound with the base present, hydrochloric acid forms metallic chlorides, the liberated acids remaining free in solution (calcium oxalate). Hydrochloric acid is also applied as a special reagent for the detection and separation of silver, mercury (of mercurous salts), and lead, and likewise for the detection of free ammonia, with which it produces in the air dense white fumes of ammonium chloride.

§ 30.

2. Chlorine (Cl) and Chlorine Water.

Preparation.—Mix 18 parts of coarse common salt with 15 parts of *finely pulverized*, good manganese dioxide, free from calcium carbonate; put the mixture into a flask, pour a *completely cooled* mixture of 45 parts of concentrated sulphuric acid (oil of vitriol) and 21 parts of water upon it, and shake the flask. A uniform and continuous evolution of chlorine gas will soon begin, which, when slackening, may be easily increased again by the application of *gentle* heat. This method of Wiggers is excellent, and can be highly recommended. To prepare chlorine water, conduct the chlorine gas evolved, first through a flask containing a little water, then into a bottle filled with cold water, and continue the process until the fluid is saturated. Where it is desired to obtain chlorine water quite free from bromine, the washing flask is changed after about one half of the chlorine has been expelled, and the gas which now passes over is conducted into a fresh bottle filled with water. If the chlorine water is to be quite free from hydrochloric acid, the gas must be passed through a U-tube containing manganese dioxide, or, according to Hampe's directions, through an aqueous solution of potassium permanganate. The chlorine water must be protected from the action of light, since, if this precaution is neglected, it speedily suffers complete decomposition, being

converted into dilute hydrochloric acid, with evolution of oxygen (resulting from the decomposition of water). Smaller quantities, intended for use in the laboratory, are best kept in a stoppered bottle, protected by a case of pasteboard, or else in a black bottle.

Small quantities of chlorine can be conveniently prepared, in an appropriate generating apparatus, by allowing hydrochloric acid, diluted with an equal volume of water, to act slowly in the cold upon cubes which are prepared, according to the directions of CL. WINKLER, from 1 part of plaster-of-Paris and 3 parts of bleaching-powder, with the addition of enough water, so that, by mixing, a moist, friable mass is produced.*

Tests.—Chlorine water must have a very strong odor of chlorine, and must volatilize completely when heated in a porcelain dish. It should contain no, or almost no, free hydrochloric acid. After having been shaken with some metallic mercury until the chlorine odor has disappeared, it should therefore give a filtrate which is at most only weakly acid. If chlorine water is shaken with carbon disulphide and finely divided zinc, the carbon disulphide should not be colored brownish red, not even transiently (bromine).

Uses.—Chlorine has a greater affinity for hydrogen and for most metals than either iodine or bromine. Chlorine water is therefore an efficient agent to effect the expulsion of iodine and bromine from their compounds. Chlorine serves, moreover, to effect the solution of certain metals (gold, platinum), to decompose metallic sulphides, to convert sulphurous acid into sulphuric acid, ferrous into ferric compounds, etc., and also to effect the destruction of organic substances, as in presence of these it withdraws hydrogen from the water, thus enabling the liberated oxygen to combine with the vegetable matters and to effect their decomposition. For the latter purpose, it is often advisable to evolve the chlorine in the fluid which contains the organic substances, and this is effected by adding hydrochloric acid to the fluid, heating the mixture, and then adding potassium chlorate. This gives rise to the formation of potassium chloride, water, free chlorine, and chlorine peroxide, which acts in a manner similar to chlorine.

* Zeitschr. f. analyt. Chem., **26**, 352.

§ 31.

3. Nitro-Hydrochloric Acid, or *Aqua regia.*

Preparation.—Mix 1 part of pure nitric acid with from 3 to 4 parts of pure hydrochloric acid.

Uses.—Nitric acid and hydrochloric acid decompose each other, the decomposition resulting in the formation of free chlorine, nitrosyl chloride, and water: $3HCl + HNO_3 = 2Cl + NOCl + 2H_2O$. This decomposition ceases as soon as the fluid is saturated with the gases, but it recommences at once when this state of saturation is disturbed by heating or by combination of the chlorine. The presence of free chlorine, and also, in a subordinate degree, that of the nitrosyl chloride, make aqua regia our most powerful solvent for metals (with the exception of those which form insoluble compounds with chlorine). Nitro-hydrochloric acid serves principally to effect the solution of gold and platinum, which are metals insoluble both in hydrochloric and in nitric acid, and also to decompose various metallic sulphides, *e.g.*, cinnabar, pyrites, etc.

§ 32.

4. Hydrofluosilicic Acid, H_2SiF_6.

Preparation.—Take 1¼ parts of powdered glass, or 1 part of powdered, ignited flint, or 1 part of quartz sand. Whichever is used, it must be washed free from every particle of dust, and then ignited. Mix intimately with 1 part of perfectly dry fluor-spar in powder,* pour 6 parts of concentrated sulphuric acid over the mixture in a retort, which it is advisable to coat with clay, and mix carefully by shaking the vessel. As the mixture swells up when getting warm, it must at first fill the retort only to one third. The neck of the retort is connected air-tight with a small tubulated receiver, and the tubulure of the latter again, by means of

* If the fluor-spar contains organic substances or metallic sulphides, it is to be previously ignited with access of air

India-rubber, with a wide glass tube bent twice at right angles. To the descending limb of the glass tube a funnel is attached by means of a rubber tube, and this funnel is lowered into a beaker containing 4 parts of water. By moderately heating the retort over charcoal or over a gas-lamp, promote the disengagement of gaseous silicon fluoride, which commences even in the cold. Towards the end of the process, a pretty strong heat should be applied. Every gas-bubble produces in the water a precipitate of silicic acid, with simultaneous formation of hydrofluosilicic acid: $3SiF_4 + 2H_2O = 2H_2SiF_6 + SiO_2$. The precipitated silicic acid renders the liquid gelatinous, and it is for this reason that the aperture of the descending limb of the tube cannot be allowed to dip directly into the water, since it would in that case speedily be choked. It sometimes happens in the course of the operation, especially towards the end, that complete channels of silicic acid are formed in the gelatinous liquid, through which, if the liquid is not occasionally stirred, the gas gains the surface without undergoing decomposition. When the evolution of gas has completely ceased, throw the gelatinous paste upon a linen cloth, squeeze the fluid through, and filter it afterwards. It is most advantageously preserved for use in bottles of hard rubber.

Tests.—Hydrofluosilicic acid must volatilize completely when heated in a platinum dish. Its dilute aqueous solution ought not to be precipitated with hydrogen sulphide, and it ought to produce no precipitate in the solution of a strontium salt (strontium sulphate).

Uses.—Bases decompose with hydrofluosilicic acid, forming water and metallic silicofluorides. Many of these are insoluble, while others are soluble. The latter may therefore be distinguished from the former by means of this reagent. In the course of analysis, hydrofluosilicic acid is applied simply for the detection and separation of barium.

c. Sulphur Acids.

§ 33.

1. Hydrogen Sulphide, *Hydrosulphuric Acid*, or *Sulphuretted Hydrogen*, H_2S.

Preparation.—Hydrogen sulphide is usually * evolved from iron sulphide, which is broken into small lumps and then treated with dilute sulphuric or hydrochloric acid. Fused iron sulphide may be purchased cheaply, or may be made by heating iron turnings, or iron nails 3 or 4 cm long, in a covered Hessian crucible to a bright red heat, and then adding

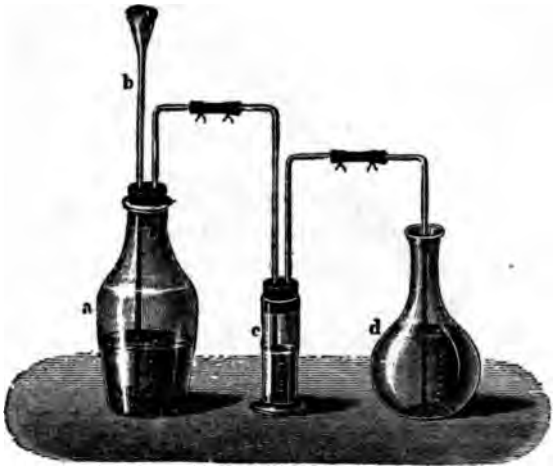

Fig. 32.

small lumps of roll-sulphur until the entire contents of the crucible are in fusion. As soon as this is the case, pour the fused mass upon sand, or into an old Hessian crucible; or make a hole in the bottom of the crucible, when the iron sulphide will run through as fast as it forms, and may be received in a shovel placed in the ash-pit; or introduce an intimate mixture of 30 parts of iron filings and 21 parts

* The evolution of hydrogen sulphide for judicial purposes will be discussed in the section which treats of the detection of poisonous metals in parts of dead bodies, etc.

of flowers of sulphur in small portions into a red-hot crucible, awaiting always the incandescence of the portion last introduced before proceeding to the addition of a fresh one. When the whole mixture has thus been put into the crucible, cover the latter closely, and expose it to a more intense heat, sufficient to make the iron sulphide fuse more or less.

The evolution of the gas may be effected in the apparatus illustrated by Fig. 32. Pour water over the iron sulphide in *a*; add concentrated hydrochloric or sulphuric acid, and shake the mixture; the evolved gas is washed in *c*. When a sufficient quantity of gas is evolved, pour the fluid off the still undecomposed iron sulphide, rinse the bottle repeatedly with water, then fill it with that fluid, and keep it for the next operation. If this precaution is neglected, the apparatus soon becomes incrusted with ferrous sulphate, and the proper evolution of gas is prevented.

For large laboratories, or for chemists having to operate often and largely with hydrogen sulphide, I recommend, if a gasometer is not preferred, the apparatus devised by BRUGNATELLI, modified as shown in Fig. 33. The bulb *B*, which is provided with a tubulure* at *a*, contains coarse pieces of glass in its neck with iron sulphide in small pieces in its body. The rubber stopper closing the neck carries on one side the tube *s* (which under certain conditions can be omitted; see below), on the other side the short tube *c*, which must be *at least a centimeter in inside diameter*, and which is united by means of a short rubber tube with the tube *d* of the same diameter, leading into the bottle *A*. The tube *e* reaches nearly to the bottom of *A*, and is connected at the other end by means of the rubber tube *f* with the bottle *M*. The latter bottle is closed by a stopper, which carries a short tube open at both ends. The stopper in the tubulure *a* of the bulb *B* carries a glass tube, which is united by means of a rubber tube to the lead pipe *q*, which carries the gas to its destination, and is provided with brass stop-cocks, *h*, *b*, *i*, *i*. To set the apparatus in operation, a mixture of 1 volume of crude

* Flasks with a tubulure at the side, such as are commonly used as receivers, as shown in BRUGNATELLI'S original drawing (Zeitschr. f. analyt. Chem., 6, 390), can also be used, but are less appropriate.

hydrochloric acid, as free as possible from arsenic, and 2 volumes of water is put into *M*, the cock *h* being opened. The liquid enters *A*, fills the bottle, and rises through *d* and

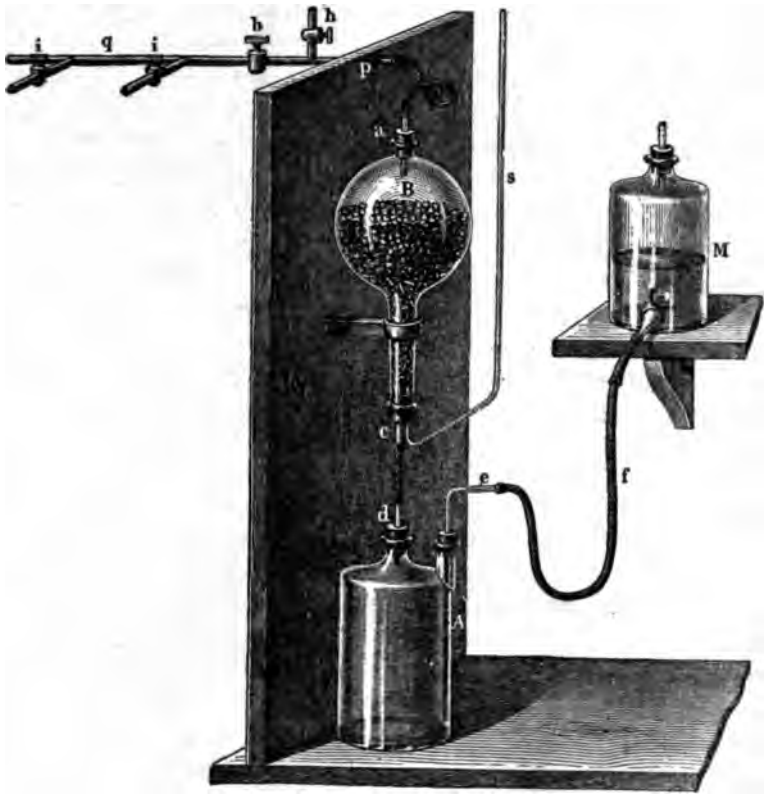

FIG. 33.

c into the bulb *B*. As soon as it has almost filled the neck, the cock *h* is closed, and care is taken that *M* is only about half filled. If the cock *b* and one of the cocks *i* are now opened, the acid rises to the iron sulphide in *B*, the evolution of hydrogen sulphide commences, and continues with great regularity, because the wide tubes *c* and *d* allow the descent of the resulting heavier ferrous chloride solution and the ascent of new acid to the iron sulphide. If it is desired to increase the contact of the acid with the iron sulphide, one or more boards are placed under *M*, thus increasing the pressure of the liquid. The stream of gas can be entirely

regulated by raising and lowering the bottle *M*, as BRUGNATELLI recommends. However, if the apparatus is to be employed for passing the gas into several liquids at the same time, as is the case in large laboratories, cocks become necessary. If the apparatus is not to be used for a considerable time, the bottle *M* is lowered. The liquid then falls in *B*, and is not in contact with the iron sulphide, so that the evolution of gas gradually ceases. If, under this condition, hydrogen sulphide is not evolved fast enough in *B* to fill the space previously occupied by the liquid, air goes in through the tube *s*. This tube, if it is used at all (see below), is made rather long in order that liquid cannot escape from it when the hydrogen sulphide gas has to overcome the pressure of a column of water of considerable height. If the iron sulphide which is moistened with acid evolves still more hydrogen sulphide after the liquid has passed down, the only consequence is that somewhat more acid flows from *A* into *M*. The tube *s* can be omitted when cocks are used. In this case, the liquid in *B* sinks more slowly when *M* is lowered, because the space occupied by the acid which flows out is filled solely by hydrogen sulphide. In the absence of a cock, however, the tube *s* is necessary, in order to avoid the sucking back of any liquid into which hydrogen sulphide is being passed at the time when *M* is lowered. By the use of cocks, this inconvenience can be easily avoided by closing *b* before lowering *M*. The gas passing out of *i*, *i* is led through wash-bottles or in winter through U-shaped tubes filled with cotton.

When the acid is finally exhausted, *M* is placed lower than *A*; while if the tube *s* has been replaced by the air-cock *h*, the latter is opened. All the liquid then goes into *M*, and can be poured out.

If a WOULFE'S bottle with three necks is used as the vessel *A*, a siphon-tube provided with a pinch-cock can be placed in the third tubulure, and the ferrous chloride solution collecting at the bottom can be allowed to flow off from time to time. In this case, the lower branch of the tube *e* should be given such a length that it reaches only half-way to the bottom of *A*, so that the hydrochloric acid flowing in does not mix with the ferrous chloride solution.

I am so well satisfied with the performance of this appara-

tus that I have given up the large lead generator which I had used for many years (see the previous editions), and have replaced it by the modified BRUGNATELLI'S generator. A lead apparatus of essentially improved construction has recently been recommended by CL. WINKLER.*

The following apparatus, devised by FR. MOHR, depends upon the same principle as the one just described, and is especially adapted for the evolution of the gas upon a smaller scale (Fig. 34). The glass vessel *A* (commonly used for desiccating gases) has a perforated disk of lead at *b*, and

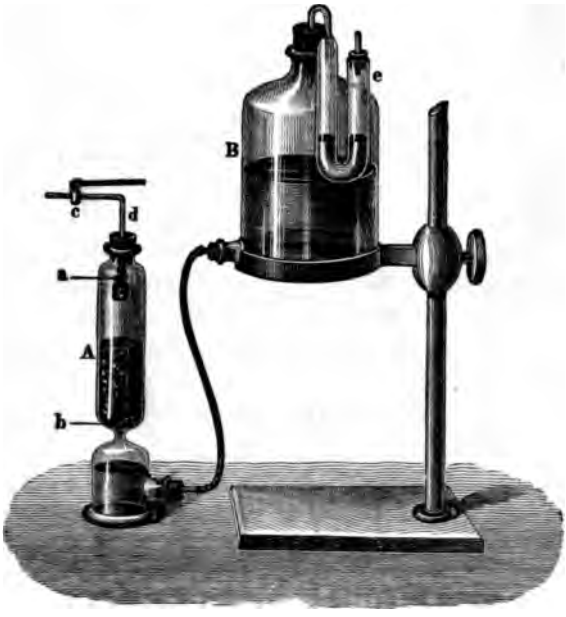

FIG. 34.

above is nearly filled with lumps of fused iron sulphide. To the end of *d* is fixed, by means of the rubber tube *a*, a small piece of wide glass tube, which is filled with cotton, and is intended to stop any particles of liquid which may be spirted up. *c* is a glass cock with a long wooden handle (which may be replaced by a pinch-cock); *e* contains a solution of sodium carbonate to prevent the escape of hydrogen

* Zeitschr. f. analyt. Chem., 21, 386.

sulphide. The acid used in *B* is a mixture of common hydrochloric acid with two measures of water.

Of the many generators which serve the same purpose, I will mention only the one proposed by POHL, which is simple and convenient in operation. It is shown in Fig. 35.

FIG. 35.

The bottle *A*, containing dilute sulphuric acid, has a capacity of from 2 to 2.5 l. In the rubber stopper *B* is the heavy glass rod *G*, the surface of the upper part of which is ground. This rod should be of at least 9 mm diameter, and should be movable by the use of some force. It carries upon its lower end the perforated basket *K* of so-called hard rubber or of porcelain. This is lined with coarse linen, and filled with pieces of iron sulphide. If the glass rod is pushed down so far that the iron sulphide just dips into the liquid, a slow stream of hydrogen sulphide results, which can be increased by pushing the basket down further, and can be interrupted by removing it from the liquid. The wide tube *R* connecting with the delivery-tube is filled with cotton, and takes the place of a wash-bottle.

Hydrogen sulphide water is usually prepared by conducting the gas into very cold water, which has been previously freed from air by boiling. The operation is continued until the water is saturated with the gas, which may be readily ascertained by closing the mouth of the flask with the thumb, and shaking it a little. If a pressure is felt from within, the operation may be considered at an end. Hydrogen sulphide water must be kept in well-closed vessels, otherwise it will soon suffer decomposition, the hydrogen being oxidized to water and a small portion of the sulphur to sulphuric acid, the rest of the sulphur separating. It keeps for a long time if put into small bottles immediately after its preparation, and these are well corked and inverted into cups filled with water.

Hydrogen sulphide water must be perfectly clear, must

strongly emit the odor of the gas, and when treated with ferric chloride it must yield a copious precipitate of sulphur. Addition of ammonia must not impart a blackish appearance to it, and upon evaporation on platinum it must leave no residue.

Uses.—Hydrogen sulphide has a strong tendency to undergo double decomposition with metallic oxides, forming water and metallic sulphides, and the latter, being mostly insoluble in water, are usually precipitated in the process. By modifying the conditions of precipitation, we may divide the whole of the precipitable metals into groups, as explained in Section III. Hydrogen sulphide is, therefore, a very valuable agent for separating the metals into the principal groups. Some of the precipitated sulphides exhibit characteristic colors indicative of the individual metals which they contain. The great facility with which hydrogen sulphide is decomposed renders this substance a useful reducing agent for many compounds. Thus, it serves to reduce ferric salts to ferrous salts, chromic acid to chromic oxide, etc. In these reductions, the sulphur separates in the form of a fine white powder. Whether it is better to apply the hydrogen sulphide in the gaseous form or in aqueous solution depends upon circumstances.

III. Bases, Metals, and Sulphides.

§ 34.

The bases are divided into oxygen bases and sulphur bases. The first are formed by the union of metals or compound radicals similar to them with oxygen, the latter from the combination of the same with sulphur.

The *oxygen bases* are classified into alkalies, alkali earths, earths proper, and oxides or hydroxides of the heavy metals. The alkalies are readily soluble in water; the alkali earths dissolve with greater difficulty in that liquid; and magnesia, the last member of the class, is only very sparingly soluble in it. The earths proper and the oxides and hydroxides of the heavy metals are insoluble in water or nearly so (except thallious hydroxide). The solutions of the alkalies and alkali earths are caustic when sufficiently concentrated; they

have an alkaline taste, change the yellow color of turmeric-paper to brown, and restore the blue tint of reddened litmus-paper; they saturate acids completely, so that even the salts which they form with strong acids do not change vegetable colors, while those with weak acids generally have an alkaline reaction. The earths proper and the oxides of the heavy metals likewise combine with acids to form salts, but, as a rule, they do not entirely take away the acid reaction of the latter.

The *sulphur bases*, which result from the combination of the metals of the alkalies and alkali earths with sulphur, are more or less soluble in water. The solutions react strongly alkaline. The remaining sulphur bases are not soluble in water. Many sulphur bases form salts with sulphur acids.

a. Oxygen Bases.

α. Alkalies.

§ 35.

1. Potassium Hydroxide, or *Caustic Potash*, KOH, and Sodium Hydroxide, or *Caustic Soda*, NaOH.

The preparation of perfectly pure caustic potash or soda is a difficult operation. In addition to perfectly pure caustic alkali, therefore, it is advisable to provide some which is not quite pure, and some which, being free from certain impurities, may in many cases be safely substituted for the pure substance.

a. Common solution of sodium hydroxide.—Put into a clean cast-iron kettle furnished with a lid, 3 parts of crystallized sodium carbonate of commerce and 15 parts of water; heat to boiling, and add, in small portions at a time, thick milk of lime prepared by pouring 3 parts of warm water over 1 part of quicklime, and letting the mixture stand in a covered vessel until the lime is reduced to a uniform mass. Keep the liquid in the kettle boiling while adding the milk of lime, and for a quarter of an hour longer; then filter off a small portion, and determine whether the filtrate still

causes effervescence in hydrochloric acid. If this is the case, the boiling must be continued, and if necessary some more milk of lime must be added to the fluid. When the solution is perfectly free from carbonic acid, cover the vessel, allow the fluid to cool a little, and then, by means of a siphon filled with water, draw off the nearly clear solution from the residuary sediment, and transfer it to a glass flask. Boil the residue a second and a third time with water and draw off the fluid in the same way. Close the mouth of the flask, and allow the lime suspended in the fluid to subside completely. Scour the iron vessel clean, pour the clear solution back into it, and evaporate it to 6 or 7 parts. The solution so prepared contains from 11 to 13 per cent of sodium hydroxide, and has a specific gravity of from 1.13 to 1.15. If it is wished to filter a solution of caustic soda which is not quite clear, a covered funnel should be used, which has been charged first with lumps of white marble and then with powder of the same, the fine dust being rinsed out with water before the filter is used (GRAEGER). Solution of caustic soda must be clear, colorless, as free as possible from carbonic acid, and ammonium sulphide must not impart a black color to it. If the lye is treated with hydrogen sulphide, then acidified with hydrochloric acid and heated, it should yield only a separation of sulphur and no colored precipitate (vanadic acid).

Traces of silicic acid, alumina, boric acid, and phosphoric acid, and small amounts of sodium chloride and sodium sulphate are usually found in a solution of caustic soda prepared in this manner, on which account it is unfit for use in accurate experiments. Commercial caustic soda, and the solutions prepared from it, usually contain some nitrate and nitrite. Solution of caustic soda is kept best in bottles closed with ground-glass caps. In default of capped bottles, common ones with well-ground stoppers may be used. In this case, the neck must be wiped perfectly dry and clean inside and the stopper coated with paraffine. If this precaution is neglected, it will be found impossible after a time to remove the stopper, particularly if the bottle is only rarely opened.

b. Potassium hydroxide purified with alcohol. — Dissolve

some commercial caustic potash in rectified alcohol, in a stoppered bottle, by digestion and shaking; let the fluid stand, decant or filter if necessary, and evaporate the clear fluid in a silver dish over the gas- or spirit-lamp until no more vapors escape, adding from time to time, during the evaporation, some water to prevent blackening of the mass. Place the silver dish in cold water until it has sufficiently cooled, remove the cake of potash from the dish, break it into coarse lumps in a hot mortar, and keep in a well-closed glass bottle. When required for use, dissolve a small piece in water.

The potassium hydroxide thus prepared is sufficiently pure for most purposes. It contains a minute trace of alumina, but is usually free from phosphoric, sulphuric, and silicic acids. The solution must remain clear upon addition of ammonium sulphide, and this solution, upon being acidified, should behave like the sodium hydroxide (see *a*); hydrochloric acid must only produce a barely perceptible effervescence in it. Upon evaporation to dryness, the solution acidified with hydrochloric acid must leave a residue which dissolves in water to a clear fluid, and when mixed with ammonia in the least possible excess, it must not show any flocks of alumina — at least until it has stood in a warm place for several hours. The solution acidified with nitric acid must not give any precipitate with a nitric acid solution of ammonium molybdate.

c. Potassium hydroxide prepared with baryta.—Dissolve pure crystals of baryta (§ 37) by heating with water, and add to the solution pure potassium sulphate until a portion of the filtered fluid, acidified with hydrochloric acid and diluted, no longer gives a precipitate on addition of a further quantity of the sulphate (16 parts of crystals of baryta require 9 parts of potassium sulphate). Let the turbid fluid clear, decant, and evaporate in a silver dish as in *b*. The caustic potash so prepared is pure, except that it contains a trifling admixture of potassium sulphate, which is mostly left behind upon dissolving in a little water. It is but rarely required, however, its use being exclusively confined to the detection of minute traces of aluminium.

Uses.—The great affinity which the fixed alkalies possess for acids renders these substances powerful agents to effect

the decomposition of the salts of most bases, and consequently the precipitation of those oxides or hydroxides which are insoluble in water. Many hydroxides thus precipitated redissolve in an excess of the precipitant, as those of aluminium, chromium, and lead; while others remain undissolved, as those of iron, bismuth, etc. The fixed alkalies, therefore, serve as a means of separating the former from the latter. Caustic potash and soda also dissolve many salts (*e.g.*, lead chromate, sulphur compounds, etc.), and thus aid in separating and distinguishing them from other substances. Many of the hydroxides and oxides precipitated by the action of potassium or sodium hydroxide exhibit peculiar colors, or possess other characteristic properties that may serve to lead to the detection of the individual metal which they respectively contain. Such are, for instance, the precipitates of manganous hydroxide, ferrous hydroxide, and mercurous oxide. The fixed alkalies expel ammonia from its salts, and enable us to detect that body by its odor, its action on vegetable colors, etc. In contact with iron and zinc or with aluminium, they cause the evolution of hydrogen, which in the nascent state converts the nitrogen of nitric and nitrous acids into ammonia, etc.

§ 36.

2. Ammonia, NH_3. Ammonium Hydroxide, NH_4OH.

Preparation.—For preparing the aqueous solution of ammonia on a small scale, the following method answers well:* Introduce into a flask 4 parts of ammonium chloride, either crystallized or in coarse powder, and the dry slaked lime prepared from 5 parts of quicklime; mix by shaking, and cautiously add enough water to make the powder agglomerate into lumps. Set the flask in a sand-bath and connect it with a wash-bottle and delivery-tube. Put a very small quantity of water in the bottle, and about 10 parts of water in the flask destined to absorb the gas. Place the latter in cold water, and then begin to apply heat. Evolution of gas

* I have described a reliable method for its preparation on a large scale in the Zeitschrift für analytische Chemie, 1, 186.

speedily sets in. Continue to heat until no more bubbles appear. Open the cork of the flask to prevent the receding of the fluid. The solution of ammonia contained in the wash-bottle is impure, but that contained in the receiver is pure; dilute the latter with water until the specific gravity is about .96 (= 10 per cent of ammonia). Keep the fluid in bottles closed with ground stoppers.

Tests.—Solution of ammonia must be colorless, and ought not to leave the least residue when evaporated in a platinum dish. When heated with an equal volume of lime-water, it should cause no turbidity—at least not to a very marked extent (carbonic acid). It must remain clear when ammonium oxalate is added to it. When supersaturated with nitric acid, it should yield a colorless solution (pyridine bases). This acidified solution should not be rendered turbid by barium nitrate or silver nitrate, nor should hydrogen sulphide impart to it the slightest color. By neutralizing it with dilute hydrochloric acid, a colorless, odorless liquid (no empyreumatic odor) must result.

Uses. — Ammonia-water is actually only a solution of ammonia in water. It is, however, sometimes convenient to assume that by the union of ammonia with water, ammonium oxide or ammonium hydroxide forms ($2NH_3 + H_2O = (NH_4)_2O$, or $NH_3 + H_2O = NH_4OH$), and that ammonia-water contains one of these. Upon this assumption, solution of ammonia may be looked upon as a fluid analogous to solutions of caustic potash and soda, which greatly simplifies the explanation of all its reactions, the salts resulting from the neutralization of acids by solution of ammonia being assumed to contain ammonium, NH_4, instead of NH_3. Ammonia is one of the reagents most frequently used. It is especially applied for the saturation of acid fluids, and also to effect the precipitation of numerous metallic hydroxides. Many of these precipitates redissolve in an excess of ammonia, as, for instance, the hydroxides of zinc, cadmium, silver, copper, etc., while others are insoluble in free ammonia. This reagent may therefore serve to separate and distinguish the former from the latter. Some of these precipitates, as well as their solutions in ammonia, exhibit peculiar colors, which may at once lead to the detection of the metal which they contain.

Many hydroxides which are precipitated by ammonia from neutral solutions are not precipitated by this reagent from acid solutions, their precipitation from the latter being prevented by the ammonium salt formed in the process. Compare § 56.

β. Alkali Earths.

§ 37.

1. Barium Hydroxide, or *Baryta*, $Ba(OH)_2$.

Preparation.—There are many ways of preparing baryta, but as witherite (barium carbonate) is now cheaply procurable, I prefer the following: Mix intimately together 100 parts of finely pulverized witherite, 10 parts of charcoal in powder, and 5 parts of rosin; put the mixture in an earthenware crucible, lute on the lid with clay, and expose the crucible so prepared to the heat of a brick-kiln. Break and triturate the baked mass, boil repeatedly with water in an iron pot, filter into bottles, stopper, and let them stand in the cold, when large quantities of crystals of barium hydroxide, $Ba(OH)_2.8H_2O$, will make their appearance. Let the crystals drain in covered funnels, dry rapidly between sheets of blotting-paper, and keep in well-closed bottles. For use, dissolve 1 part of the crystals in 20 parts of water, with the aid of heat, and filter the solution. The *baryta-water* so prepared is purer than the mother-liquor running off from the crystals. The residue, which is insoluble in water and consists of undecomposed witherite and charcoal, may be turned to account in the preparation of barium chloride.

Tests.—Baryta-water must, after precipitation of the barium by pure sulphuric acid, give a filtrate remaining clear when mixed with alcohol and leaving no fixed residue upon evaporation in a platinum crucible. After addition of acetic acid to acid reaction, it ought not to be colored nor precipitated by hydrogen sulphide.

Uses.—Barium hydroxide being a strong base precipitates the metallic hydroxides insoluble in water from the solutions of their salts. In the course of analysis, we use it especially

to precipitate magnesia. Baryta-water may also be used to precipitate those acids which form insoluble barium compounds. With this in view, it is applied to effect the detection of carbonic acid, the removal of sulphuric acid, phosphoric acid, etc.

§ 38.

2. Calcium Hydroxide, or *Lime*, $Ca(OH)_2$.

Use is made of—

a. Calcium hydroxide in the form of a fine powder. *b. Lime-water.*

Calcium hydroxide is obtained by slaking lumps of pure calcined lime in a porcelain dish with half their weight of water. The heat which accompanies the combination of the lime and the water is sufficient to evaporate the excess of water. Slaked lime must be kept in a well-stoppered bottle.

To prepare *lime-water*, digest slaked lime for some time with cold distilled water, shaking the mixture occasionally; let the undissolved portion of lime subside, decant, and keep the clear fluid in a well-stoppered bottle. If it is wished to have the lime-water quite free from all traces of alkalies, baryta, and strontia, which are almost invariably present in slaked lime prepared from calcined limestone, the liquids of the first two or three decantations must be removed, and the fluid decanted afterwards alone used.

Tests.—Lime-water must impart a strongly marked brown tint to turmeric-paper, and give a not too inconsiderable precipitate with sodium carbonate. It speedily loses these properties upon exposure to the air, and is thereby rendered totally unfit for analytical purposes.

Uses.—With many acids, lime forms insoluble salts; with others, soluble salts. Lime-water may therefore serve to distinguish the former acids, which it precipitates from their solutions, from the latter, which it will of course fail to precipitate. Many of the precipitable acids are thrown down only under certain conditions, *e.g.*, on boiling (citric acid), which affords a ready means of distinguishing between them by altering these conditions. We use lime-water in analysis

principally to effect the detection of carbonic acid, and also to distinguish between citric acid and tartaric acid. Slaked lime is chiefly used to liberate ammonia from ammonium salts.

γ. Heavy Metals and their Oxides and Hydroxides.

§ 39.

1. Zinc, Zn.

Zinc of good quality should be selected, which dissolves in sulphuric acid completely or leaves only a very slight residue, and which contains no arsenic. The latter impurity must be tested for by methods given in Section III, under reactions for arsenious acid. Fuse the metal and pour it in a thin stream into a large vessel of water. Zinc which contains arsenic must be rejected, for no practicable process of purification is known (Eliot and Storer).*

Uses.—In qualitative analysis, zinc serves for the evolution of hydrogen, and also of hydrogen arsenide and antimonide. It is occasionally used also to precipitate some metals from their solutions, in which process the zinc simply displaces the other metal: $CuSO_4 + Zn = ZnSO_4 + Cu$. Zinc is also sometimes used for the detection of sulphurous acid and phosphorous acid, and it must then be tested for zinc sulphide or zinc phosphide, as the case may be. For the manner of using and the testing, see Section III, under the reactions for sulphurous and phosphorous acids.

2. Aluminium, Al.

Aluminium may serve for precipitating many metals from their solutions, but is employed especially for the reduction of nitric acid, sulphurous acid, and other oxygen salts. It is used in the form of fine drillings. It must dissolve in potas-

* According to Gunning (Scheikundige Bijdragen, Deel I, Nr. I, p. 113), the purification may be effected by repeated fusion with a mixture of sodium carbonate and sulphur; according to Selmi (Zeitschr. f. analyt. Chem., **22**, 76), by treating molten zinc with ammonium chloride; according to Lescoeur (Compt rend., **116**, 58), by first fusing with potassium nitrate, then with zinc chloride

sium hydroxide without leaving a residue. The hydrogen gas thus evolved ought not to blacken papers moistened with silver nitrate or lead acetate.

3. Iron, Fe.

Iron reduces many metals, and precipitates them from their solutions in the metallic state. We use it especially for the detection of copper, which precipitates upon it with its characteristic color. Any clean surface of iron, such as a knife-blade, a needle, a piece of wire, etc., will serve for this purpose.

4. Copper, Cu.

We use copper to effect the reduction of mercury, and sometimes, also, for the deposition of arsenic. Any bright copper surface (sheet or wire) can be used for the experiments.

§ 40.

5. Bismuth Hydroxide, BiOOH.

Preparation. — Dissolve bismuth, freed from arsenic by fusion with sodium sulphide (*hepar sulphuris*), in dilute nitric acid; dilute the solution till a slight permanent precipitate is produced, filter, and evaporate the filtrate to crystallization. Wash the crystals with water containing nitric acid, triturate them with water, add ammonia in excess, and let the mixture digest for some time; then filter, wash, dry the white precipitate, and keep it for use.

Tests.—The bismuth hydroxide (instead of which basic bismuth nitrate may be used if it is entirely free from arsenic and antimony) is dissolved in dilute nitric acid, and precipitated with hydrogen sulphide. Part of the precipitated sulphide is treated with ammonia and filtered, and part is treated with ammonium sulphide and filtered. These filtrates are then mixed with hydrochloric acid in excess. The first should give no precipitate, and the second only a white precipitate of sulphur.

Uses.—When boiled with alkaline solutions of metallic

sulphides, bismuth hydroxide reacts with the latter, giving rise to the formation of metallic oxides and bismuth sulphide. We use this reagent principally to convert arsenious sulphide and arsenic sulphide into arsenious and arsenic acids.

b. Sulphides.

§ 41.

1. Ammonium Sulphide, $(NH_4)_2S$.

We use in analysis—

a. Colorless ammonium monosulphide.

b. Yellow ammonium polysulphide.

Preparation. — Transmit hydrogen sulphide through 3 parts of ammonia solution until no further absorption takes place, then add 2 parts of the same ammonia solution. The action of hydrogen sulphide upon ammonia gives rise to the formation, first, of $(NH_4)_2S$, then of NH_4SH. Upon addition of the same quantity of solution of ammonia as has been saturated, the ammonia reacts with the ammonium hydrosulphide, and ammonium sulphide is formed. The rule, however, is to add only two thirds of the quantity of solution of ammonia, as it is better that the preparation should contain a little ammonium hydrosulphide than that free ammonia should be present. To employ ammonium hydrosulphide instead of the simple sulphide is unnecessary, and tends to increase the smell of hydrogen sulphide in the laboratory, for the compound allows that gas to escape when acting upon acid sulphides.

Ammonium sulphide should be kept in well-corked phials. It is colorless at first, and deposits no sulphur upon addition of acids. Upon exposure to the air, however, it acquires a yellow tint, owing to the formation of ammonium disulphide, which is attended also with formation of ammonia and water: $2(NH_4)_2S + O = (NH_4)_2S_2 + 2NH_3 + H_2O$. Continued action of the oxygen of the air upon the ammonium sulphide tends at first to the formation of still higher sulphides, but afterwards the fluid deposits sulphur; finally all the ammonium sulphide is decomposed, and the solution contains noth-

ing but ammonia and ammonium thiosulphate. The formation of thiosulphate proceeds as follows: $(NH_4)_2S_5 + 3O = (NH_4)_2S_2O_3$.

The ammonium sulphide which has turned yellow by moderate exposure to the air may be used for all purposes requiring the employment of yellow ammonium sulphide. The yellow sulphide may also be expeditiously prepared by digesting the monosulphide with some sulphur. All kinds of yellow ammonium sulphide deposit sulphur, and look turbid and milky on being mixed with acids.

Tests.—Ammonium sulphide must strongly emit the odor peculiar to it, and with acids it must evolve abundance of hydrogen sulphide. The evolution of gas may be attended by the separation of a pure white precipitate, but no other precipitate must be formed. Upon evaporation and exposure to a red heat in a platinum dish, it must leave no residue. Even on heating, it must not precipitate or render turbid solution of magnesium sulphate or solution of calcium chloride (free ammonia, ammonium carbonate).

Uses.—Ammonium sulphide is one of the reagents most frequently employed. It serves (*a*) to effect the precipitation of those heavy metals which hydrogen sulphide fails to throw down from acid solutions, *e.g.*, iron, cobalt, etc.: $(NH_4)_2S + FeSO_4 = FeS + (NH_4)_2SO_4$; (*b*) to separate the metallic sulphides thrown down from acid solutions by hydrogen sulphide, since it dissolves some of them to sulphur salts, as the sulphides of arsenic and antimony, etc., leaving others undissolved—for instance, lead sulphide, cadmium sulphide, etc. The ammonium sulphide used for this purpose must contain an excess of sulphur if the metallic sulphides to be dissolved will dissolve only as higher sulphides. For example, stannous sulphide, SnS, dissolves with ease only after being changed to stannic sulphide, SnS_2.

From solutions of aluminium and chromium salts, ammonium sulphide precipitates hydroxides, with escape of hydrogen sulphide, as the sulphur compounds corresponding to these hydroxides cannot form in the wet way: $Al_2(SO_4)_3 + 3(NH_4)_2S + 6H_2O = Al_2(OH)_6 + 3(NH_4)_2SO_4 + 3H_2S$. Salts insoluble in water are thrown down by ammonium sulphide unaltered from their solutions in acids. For instance, calcium

phosphate is thus precipitated from its solution in hydrochloric acid.

§ 42.

2. Sodium Sulphide, Na_2S.

Preparation.—The same as ammonium sulphide, except that solution of caustic soda is substituted for solution of ammonia. Filter, if necessary, and keep the fluid in well-stoppered bottles. If required to contain some higher sulphide of sodium, digest with powdered sulphur. When hydrochloric acid is added to the solution which has been somewhat diluted with water, there must be an abundant evolution of hydrogen sulphide. In this case, there ought to occur, according to the degree of sulphurization of the sodium sulphide, either no precipitate or only a white precipitate of sulphur (vanadic acid, bases of the sixth group).

Uses.—Sodium sulphide is sometimes substituted for ammonium sulphide to effect the complete separation of cupric sulphide from sulphur compounds soluble in alkaline sulphides, *e.g.*, from stannic sulphide, as cupric sulphide is not quite insoluble in ammonium sulphide.

IV. Peroxides.

§ 43.

1. Hydrogen Peroxide, H_2O_2.

Hydrogen peroxide is best procured by purchase. The clear, colorless liquid employed for medicinal purposes is adapted for use in qualitative analysis. It is an aqueous solution of hydrogen peroxide which is usually slightly acidified with hydrochloric or sulphuric acid for the sake of durability, and it contains about 3 per cent by weight of the substance.

Tests.—Hydrogen peroxide must be completely volatilized by heating, and when it is mixed with a solution of potassium permanganate, the latter should be decolorized, and there

should be a large amount of effervescence, due to an abundant evolution of oxygen. The last test is to be repeated from time to time in order to determine whether the hydrogen peroxide has not become decomposed.

Uses.—Hydrogen peroxide is of use in qualitative analysis principally as an oxidizing agent, and for this purpose offers the advantage that no elements other than hydrogen and oxygen are added to the liquid under treatment, except the small amount of acid contained in the reagent.

§ 44.

2. Lead Dioxide, PbO_2.

Preparation.—The rather small quantity of lead peroxide that is used in qualitative analysis is most easily prepared by digesting red lead (which should give a clear solution with dilute nitric acid and alcohol) with an excess of dilute nitric acid. A precipitate of brown lead dioxide and a solution containing lead nitrate are thus obtained. The precipitate is collected upon a filter, completely washed with hot water, and dried at a gentle heat.

Tests.—These are to be directed especially to the detection of manganese. To make an accurate test for this, a sample is heated with pure concentrated sulphuric acid until complete decomposition takes place, and until the excess of sulphuric acid has been almost completely removed; then, after cooling, a further portion of the lead peroxide is added, heated with a mixture of about equal parts of nitric acid (sp. gr. 1.2) and water, and allowed to settle. The liquid above the precipitate ought to show no red coloration due to permanganic acid.

Uses.—Lead dioxide serves especially for the conversion of manganese compounds into permanganic acid, and on account of the high coloring power of the latter, it offers a very delicate and characteristic reagent for the detection of manganese.

V. Salts.

Of the many salts employed as reagents, those of potassium, sodium, and ammonium, are principally used on account of their acids. Therefore, salts of sodium may often be substituted for the corresponding potassium salts, etc., and it is almost always immaterial whether we use sodium carbonate or potassium carbonate, potassium ferrocyanide or sodium ferrocyanide, etc. I have therefore here classified the salts of the alkali metals *by their acids*. With the salts of the alkali-earth metals and those of the heavy metals, however, the case is different. These are not used for their acids, but for their bases, and we may often substitute for one salt of a metal another similar one, as barium nitrate or acetate for barium chloride, etc. For this reason, I have classified the salts of the alkali-earth metals and of the heavy metals *by their bases.*

a. Salts of the Alkali Metals.

§ 45.

1. Potassium Sulphate, K_2SO_4.

Preparation and Tests.—Purify potassium sulphate of commerce by recrystallization, and dissolve 1 part of the pure salt in 12 parts of water. The solution should be neutral, and should be neither made turbid nor precipitated by hydrogen sulphide, ammonium sulphide, ammonium oxalate, or silver nitrate. By testing with ferrous sulphate or diphenylamine, it must show itself to be free from nitric acid. (See the reactions of nitric acid in Section III.)

Uses.—Potassium sulphate serves to detect and separate barium and strontium. It is in many cases used in preference to dilute sulphuric acid, which is employed for the same purpose, as it does not, like the latter reagent, disturb the neutrality of the solution.

§ 46.

2. Hydrogen Disodium Phosphate, or *Sodium Phosphate*, $HNa_2PO_4.12H_2O$.

Preparation.—Purify the commercial salt by recrystallization, and dissolve 1 part of the pure salt in 10 parts of water for use.

Tests.—Solution of sodium phosphate must not become turbid when heated with ammonia. The precipitates which solution of barium nitrate and solution of silver nitrate produce in it must dissolve completely, and without effervescence, upon addition of dilute nitric acid. Even after heating, hydrogen sulphide ought not to color or precipitate the solution, either as it is or after acidifying it with hydrochloric acid.

Uses.—Sodium phosphate precipitates the alkali-earth metals and all the heavy metals from solutions of their salts. In the course of analysis, after the separation of the heavy metals, it serves as a test for alkali-earth metals in general; and, after the separation of barium, strontium, and calcium, as a special test for the detection of magnesium. For the latter purpose, it is used in conjunction with ammonia, the magnesium precipitating as ammonium magnesium phosphate. In the place of sodium phosphate, sodium ammonium phosphate (§ 89) or ammonium phosphate, $H(NH_4)_2PO_4$, can be used.

§ 47.

3. Ammonium Oxalate, $(NH_4)_2C_2O_4.H_2O$.

Preparation.—1 part of commercial oxalic acid (which generally contains potassium) is dissolved in 6 parts of water at the boiling temperature. This is allowed to cool, and the solution is poured off or filtered from the oxalic acid crystals, which usually contain potassium tetra-oxalate; it is evaporated further, again cooled, and thus are obtained a second and third crop of oxalic acid which are almost or quite free from potassium. The mother-liquor, together with the first crystallization, may be used for the preparation of potassium

or sodium oxalate. The pure crystals are dissolved in 2 parts of distilled water by warming, ammonia-water is added to distinct alkaline reaction, and the solution is then put in a cold place. The crystals which form are drained, and a further crystallization is obtained by properly evaporating the mother-liquor. The crystals are purified by recrystallization. For use, 1 part of the pure salt is dissolved in 24 parts of water.

Tests.—The solution of ammonium oxalate must not be precipitated or rendered turbid by hydrogen sulphide, or by ammonium sulphide. Ignited on platinum, the salt must volatilize without leaving a residue. The precipitates produced in the solution by barium chloride and by silver nitrate must be completely soluble in nitric acid.

Uses.—With calcium, strontium, barium, lead, and other metals, oxalic acid forms insoluble or very difficultly soluble compounds. Ammonium oxalate produces, therefore, in the aqueous solutions of the salts of these bases, precipitates of the corresponding oxalates. In analysis, the reagent serves principally for the detection and separation of calcium.

§ 48.

4. Sodium Acetate, $NaC_2H_3O_2.3H_2O$.

Preparation.—Dissolve crystallized sodium carbonate in a little water, add to the solution acetic acid in slight excess, evaporate to crystallization, and purify the salt by recrystallization. This salt can now be procured very pure in commerce. For use dissolve 1 part of the salt in 10 parts of water.

Tests.—Sodium acetate must be colorless and free from empyreumatic matter and inorganic acids. The solution ought not to be colored, made turbid, nor precipitated by hydrogen sulphide, ammonium sulphide, ammonium oxalate, barium chloride, or, after diluting and acidifying with nitric acid, by silver nitrate.

Uses.—The stronger acids in the free state decompose sodium acetate, combining with the base and setting the acetic acid free. In the course of analysis, sodium acetate is used principally to precipitate ferric phosphate (which is insoluble in acetic acid) from its solution in hydrochloric acid. It serves,

also, to effect the separation of ferric oxide and alumina, which it precipitates on boiling from the solutions of their salts.

§ 49.

5. Sodium Carbonate, Na_2CO_3; *crystallized*, $Na_2CO_3.10H_2O$.

Preparation.—Finely pulverize "bicarbonate of soda" of commerce, put the powder into a funnel stopped loosely with cotton, make the surface even, cover it with a disk of thick filter-paper with turned-up edges, and wash by pouring small quantities of water on the paper disk until the filtrate, when acidified with nitric acid, is not rendered turbid by solution of silver nitrate, or by solution of barium chloride. Let the salt dry, and then convert it by gentle ignition into the normal carbonate. This is effected best in a vessel of silver or platinum, but it may be done also in a perfectly clean iron dish, or, on a small scale, in one of porcelain. Dissolve 1 part of the anhydrous, or 2.7 parts of the crystallized, salt in 5 parts of water for use.

Tests.—Sodium carbonate should be absolutely white, and should dissolve in water to a clear solution. Its solution should not decolorize water which is colored reddish by potassium permanganate (sodium thiosulphate). After acidifying with nitric acid, neither barium chloride nor silver nitrate should cause turbidity in the solution, nor should it become yellow or give a precipitate of this color when warmed with ammonium molybdate and nitric acid. When supersaturated with hydrochloric acid, evaporated to dryness, and dissolved again in water, no residue should be left (silicic acid). The solution when acidified with hydrochloric acid ought not to be colored nor precipitated by hydrogen sulphide, or, after addition of ammonia, by ammonium sulphide. The solution to which barium chloride has been added in excess ought not to react alkaline (sodium hydroxide). When fused with potassium cyanide in a porcelain boat within a glass tube through which a slow stream of dry carbonic acid gas is passed, it ought to give no trace of a dark sublimate (arsenic). (Compare the reactions of arsenious acid in Section III.)

Uses.—With the exception of the alkali metals, sodium

carbonate precipitates all the metals in the form of normal or basic carbonates. Those metals which form soluble acid carbonates require boiling for their complete precipitation from acid solutions. Many precipitates produced by the action of sodium carbonate exhibit a characteristic color, which may lead to the detection of the individual metals that they respectively contain. Solution of sodium carbonate also serves for the decomposition of many insoluble salts, more particularly of those with organic acids. Upon boiling with sodium carbonate, these salts are converted into insoluble carbonates, while the acids combine with the sodium, and are thus obtained in solution. Sodium carbonate is often used also to saturate free acids.

§ 50.

6. Ammonium Carbonate, $(NH_4)_2CO_3$.

Preparation.—Take commercial "carbonate of ammonia" entirely free from any smell of animal oil, such as is prepared on a large scale by sublimation from a mixture of ammonium chloride and calcium carbonate, carefully scrape off the outer and inner surface of the mass, if necessary, and dissolve 1 part of the salt by digestion with 4 parts of water to which 1 part of ammonia solution has been added.

Tests.—Pure ammonium carbonate must completely volatilize. Its solution ought not to be colored or precipitated by ammonium sulphide. It must yield a colorless solution when supersaturated with nitric acid (pyridine bases). The solution, thus acidified, ought to be colored or precipitated neither by barium nor silver solution, nor by hydrogen sulphide.

Uses.—Like sodium carbonate, ammonium carbonate precipitates most metals. It is generally employed in preference to the former reagent, because it introduces no non-volatile body into the solution. Complete precipitation of many of the metals takes place only on boiling, and several of the precipitates redissolve in an excess of the precipitant. In like manner, ammonium carbonate dissolves many hydroxides and sulphides, and thus enables us to distinguish

and separate them from others which are insoluble in this reagent.

Ammonium carbonate, like ammonia solution, and for the same reason, fails to precipitate from acid solutions many metals which it precipitates from neutral solutions. (Compare § 36.) We use ammonium carbonate in analysis principally to effect the precipitation of barium, strontium, and calcium, and the separation of these substances from magnesium; also, to separate arsenious sulphide, which is soluble in it, from antimonious sulphide, which is insoluble.

§ 51.

7. Hydrogen Sodium Sulphite, $HNaSO_3$.

Preparation.—Heat 5 parts of copper tacks or clippings with 20 parts of concentrated sulphuric acid in a flask, and conduct the sulphur dioxide gas evolved, first through a washing-bottle containing some water, then into a flask containing 4 parts of purified sodium bicarbonate (§ 49), or 7 parts of pure crystallized, normal sodium carbonate, and from 20 to 30 parts of water (this flask should not be much more than half full); continue the transmission of the gas until the evolution of carbon dioxide ceases. Keep the solution, which has a strong smell of sulphurous acid, in a well-stoppered bottle.

Tests.—Acid sodium sulphite, when evaporated to dryness with pure sulphuric acid, while evolving a copious amount of sulphurous acid, must leave a residue, the aqueous solution of which is not altered by hydrogen sulphide after the addition of some hydrochloric acid, nor precipitated yellow by heating with a solution of ammonium molybdate mixed with nitric acid.

Uses.—Sulphurous acid has a great tendency to pass to the state of sulphuric acid by absorbing oxygen. It is therefore one of our most powerful reducing agents. Acid sulphite of sodium, which has the advantage of being less readily decomposed than sulphurous acid, acts in the same manner upon addition of acid. We use it principally to reduce arsenic acid to arsenious acid, chromic acid to a

chromic salt, and ferric salts to ferrous salts; also for the precipitation of selenium from selenious acid, etc.

§ 52.

8. Potassium Nitrite, KNO_2.

Preparation.—In an iron pan fuse 1 part of potassium nitrate, add 2 parts of lead, and stir constantly with an iron rod. Even at a low red heat, the lead becomes for the most part oxidized and converted into a yellow powder. To oxidize the remainder, the heat is increased to visible redness and maintained at that point for half an hour. Allow the mass to cool, treat with cold water, filter, and pass carbon dioxide through the filtrate. This precipitates almost the whole of the lead in solution, and the remainder is removed with a little hydrogen sulphide. After filtering, concentrate the liquid to a small volume, let the undecomposed potassium nitrate crystallize out, evaporate to dryness, with stirring at the last stage of the process, and heat to fusion in order to destroy any potassium thiosulphate that may have been formed (Aug. Stromeyer).

Tests.—Upon addition of dilute sulphuric acid, potassium nitrite must copiously evolve nitric oxide gas. Its dilute solution when mixed with ammonia and ammonium sulphide ought not to be colored or precipitated.

Uses.—Potassium nitrite is an excellent means to effect the detection and separation of cobalt, in the solutions of which metal it produces a precipitate of potassium cobaltic nitrite. In presence of free acid it also serves to liberate iodine from its compounds.

§ 53.

9. Potassium Chromate, K_2CrO_4.

Preparation and Tests.—Recrystallize commercial potassium dichromate several times, dissolve 60 parts of the dry salt in 300 parts of boiling water, add 28.1 parts of pure dry

potassium carbonate, and evaporate to crystallization. Dissolve 1 part of the yellow crystals thus obtained in 10 parts of water.

The solution of potassium chromate, when heated with hydrochloric acid and some alcohol, must yield a green solution, which, after neutralizing the greater part of the free acid with ammonia, must not be made turbid by the addition of barium chloride (sulphate). The reaction of potassium chromate should be only faintly alkaline.

Uses.—Potassium chromate reacts with many of the soluble metallic salts. Most of the precipitated chromates are very sparingly soluble, and often show characteristic colors, so that the metals are thereby easily recognized. We make use of potassium chromate especially for testing for lead, and it is also employed for distinguishing and separating barium and strontium. Potassium dichromate can be frequently used instead of the chromate.

§ 54.

10. Potassium Pyroantimonate, $H_2K_2Sb_2O_7.6H_2O$.

Preparation.—Project a mixture of equal parts of pulverized tartar-emetic and potassium nitrate in small portions at a time into a red-hot crucible. After the mass has deflagrated, keep it at a moderate red heat for a quarter of an hour. It froths at first, but after some time will be in a state of calm fusion. Remove the crucible from the fire, let the mass get nearly cold, and extract it with warm water. Transfer to a suitable vessel by rinsing, and decant the clear fluid from the heavy white powder deposited (Brunner). Wash this with some cold water, heat 1 part with 200 parts of water for a short time to boiling, cool, and filter.

Tests and Uses. — Acid potassium pyroantimonate is sparingly soluble in water, requiring 90 parts of boiling and 250 parts of cold water for solution. The solution prepared according to the above directions keeps for quite a long time unchanged. It must be clear and of neutral reaction. It ought not to give a precipitate with potassium chloride, nor with ammonium chloride, but with sodium chloride solution,

it must yield a crystalline precipitate. When mixed with an equal volume of concentrated sulphuric acid and cooled, no brown zone ought to form when a solution of ferrous sulphate is placed above the mixture (nitrous or nitric acid). Acid potassium pyroantimonate, generally called simply potassium antimonate, serves as a very good reagent for sodium, but its employment requires great caution (see § 94).

§ 55.

11. Ammonium Molybdate, $(NH_4)_2MoO_4$, dissolved in Nitric Acid—Molybdic Acid Solution.

Preparation and Tests.—Triturate molybdenite with about an equal bulk of coarse quartz sand washed with hydrochloric acid until it is reduced to a moderately fine powder; heat to faint redness, with repeated stirring, until the mass has acquired a lemon-yellow color (which after cooling turns white). With small quantities, this operation may be conducted in a flat platinum dish; with large quantities, in a muffle. Extract with solution of ammonia, filter, evaporate the filtrate, heat the residue to faint redness until it appears yellow or white, and then digest for several days with nitric acid on the water-bath, in order to convert any phosphoric acid present to the tribasic state. When the nitric acid is evaporated, dissolve the residue (in the place of which the commercial, pure molybdic acid can also be used) in 4 parts of solution of ammonia, filter rapidly, and pour the filtrate into 15 parts by weight of nitric acid of 1.20 sp. gr.

To prepare the reagent from ammonium molybdate, dissolve 150 g of the pulverized, pure salt in 1 liter of water by heating, and pour the solution into 1 liter of nitric acid of 1.20 sp. gr. Keep the mixture standing several days in a moderately warm place, which will cause the separation of any remaining traces of phosphoric acid as ammonium phosphomolybdate. Decant the colorless fluid from the precipitate, and keep it for use. Heated to 40°, the liquid remains clear. When heated to boiling, it ought not to give a yellow precipitate. The white precipitate which then separates is molybdic acid or an acid ammonium molybdate. The yellow

precipitate which sometimes separates from the solution upon long keeping is a modification of molybdic acid.

Uses.—Phosphoric acid and arsenic acid form with molybdic acid and ammonia peculiar, yellow compounds which are almost absolutely insoluble in the nitric acid solution of ammonium molybdate. The phosphoric acid compound is formed in the cold, but the production of the arsenic acid compound requires heat. Ammonium molybdate therefore affords an excellent means for detecting these acids, but more especially for finding very minute quantities of phosphoric acid in acid solutions containing aluminium and alkali-earth metals.

§ 56.

12. Ammonium Chloride, NH_4Cl.

Preparation.—Select sublimed white sal-ammoniac of commerce. If it contains iron it must be purified. For this purpose, chlorine-water is added to the boiling solution until any ferrous chloride present is changed to ferric chloride. Ammonia is then added in slight excess, the whole is heated until the liquid is scarcely alkaline, the resulting precipitate is allowed to settle, the liquid is then filtered and evaporated to crystallization. Dissolve 1 part of the salt in 8 parts of water for use.

Tests.—Upon evaporation on platinum, solution of ammonium chloride must leave a residue, which upon further heating volatilizes completely. Ammonium sulphide should have no action upon the solution, and barium chloride should not cause a turbidity in it. Ferric chloride ought not to redden it when acidified with hydrochloric acid (ammonium sulphocyanide). When evaporated with nitric acid upon the water-bath, the ammonium chloride solution must leave a white residue, not a yellowish or reddish one (pyridine bases). Its reaction must be neutral.

Uses.—Ammonium chloride is used very frequently in analysis. It serves principally to retain in solution certain oxides, *e.g.*, manganous and magnesium oxides, or salts, *e.g.*, calcium tartrate, upon the precipitation of other oxides or

salts by ammonia or some other reagent. This application of ammonium chloride is based upon the tendency of the ammonium salts to form double compounds with other salts. Ammonium chloride also serves to distinguish between precipitates possessing similar properties in other respects; for instance, to distinguish the ammonium magnesium phosphate, which is almost insoluble in ammonium chloride, from other magnesian precipitates. It is likewise used to precipitate from their solutions in potassium hydroxide, various substances which are soluble in that alkali, but insoluble in ammonia, *e.g.*, alumina, chromic oxide, etc. In this process, the elements of the ammonium chloride transpose with those of the caustic potash, and potassium chloride, water, and ammonia are formed. Ammonium chloride is also applied as a special reagent to effect the precipitation of platinum as ammonium platinic chloride.

§ 57.

13. Potassium Cyanide, KCN.

Preparation.—Heat potassium ferrocyanide of commerce (perfectly free from potassium sulphate) gently, with stirring, until the water of crystallization is completely expelled; triturate the anhydrous mass, and mix 8 parts of the dry powder with 3 parts of perfectly dry potassium carbonate; fuse the mixture in a covered Hessian, or, better still, in a covered iron, crucible until the mass is at a faint red heat, appears clear, and a sample of it, taken out with a heated glass or iron rod, looks perfectly white. Remove the crucible from the fire, tap it gently, and let it cool a little until the evolution of gas has ceased. Pour the fused potassium cyanide into a heated, tall, crucible-shaped vessel of clean iron or silver, or into a moderately hot Hessian crucible, using proper care to prevent the running out of any of the minute particles of iron carbide which have separated in the process of fusion and have subsided to the bottom of the crucible. Let the mass now slowly cool in a somewhat warm place. The potassium cyanide thus prepared is very well adapted for analytical purposes, although it contains potassium carbonate and cyanate,

the latter upon solution in water being transformed into ammonium carbonate and potassium carbonate: $2KCNO + 4H_2O = K_2CO_3 + (NH_4)_2CO_3$. Keep the potassium cyanide (which, as well known, is very poisonous) in the solid form in a well-stoppered bottle, and dissolve 1 part of it in 4 parts of water, without application of heat, when required for use. Instead of potassium cyanide, the sodium-potassium cyanide, which is at present extensively prepared, can be used. This is made in the same manner as potassium cyanide, by fusing together 4 parts of dehydrated potassium ferrocyanide with 1 part of pure anhydrous sodium carbonate.

Tests.—Potassium cyanide must be of a milk-white color, and quite free from particles of iron or charcoal. It must completely dissolve in water to a clear fluid. It must contain neither silica nor potassium sulphide. The precipitate which lead salts produce in its solution must accordingly be of a white color, and the residue which its solution leaves upon evaporation, after previous supersaturation with hydrochloric acid,* must completely dissolve in water to a clear fluid. When fused with pure sodium carbonate in a porcelain boat within a glass tube through which is passed a slow stream of dry carbonic acid, it ought to give no trace of an arsenic mirror. (Compare § 49.)

Uses.—Potassium cyanide prepared in the manner described produces in the solutions of most metallic salts, precipitates of cyanides of metals or of hydroxides or carbonates which are insoluble in water. The precipitated cyanides are soluble in potassium cyanide, and by further addition of the reagent may therefore be separated from the hydroxides or carbonates which are insoluble in potassium cyanide. Some of the metallic cyanides redissolve invariably in the potassium cyanide as double cyanides, even in the presence of free hydrocyanic acid and upon boiling; while others combine with cyanogen to new radicals, which remain in solution in combination with the potassium. The most common compounds of this nature are potassium cobalticyanide and potassium ferro- and ferricyanide. These differ from the double

* This supersaturation with hydrochloric acid is attended with disengagement of hydrocyanic acid.

cyanides of the other kind particularly in this, that dilute acids fail to precipitate the metallic cyanides which they contain. Potassium cyanide may accordingly serve to separate the metals which form compounds of the latter description from others, the cyanides of which are precipitated by acids from their solution in potassium cyanide. In the course of analysis, this reagent is of great importance, as it serves to effect the separation of cobalt from nickel; also that of copper, the sulphide of which metal is soluble in it, from cadmium, whose sulphide is insoluble.

§ 58.

14. Potassium Ferrocyanide, $K_4Fe(CN)_6.3H_2O$.

Preparation.—The potassium ferrocyanide found in commerce is sufficiently pure. 1 part of the salt is dissolved in 12 parts of water for use.

Uses.—Ferrocyanogen forms with most metals compounds insoluble in water, some of which exhibit highly characteristic colors. These ferrocyanides are produced when potassium ferrocyanide is brought into contact with soluble metallic salts, the potassium changing places with the other metals. The cupric and ferric ferrocyanides exhibit the most characteristic colors. Potassium ferrocyanide therefore serves particularly as a test for cupric and ferric compounds.

§ 59.

15. Potassium Ferricyanide, $K_6Fe_2(CN)_{12}$.

Preparation.—Conduct chlorine gas slowly into a solution of 1 part of potassium ferrocyanide in 10 parts of water, with frequent stirring, until the solution exhibits a fine deep-red color by transmitted light (the light of a candle answers best), and a portion of the fluid produces no longer a blue precipitate in a solution of ferric chloride, but imparts a brownish tint to it. Evaporate the fluid in a dish to $\frac{1}{4}$ of its weight and let it crystallize. The mother-liquor will upon further evaporation yield a second crop of crystals fit for use. Dissolve

the whole of the crystals obtained in 3 parts of water, filter if necessary; evaporate the solution briskly to half its volume, and let it crystallize again. Dissolve some of the magnificent red crystals in a little water, preferably just before use. The solution, which decomposes under the influence of daylight with the deposition of a blue precipitate and the formation of potassium ferrocyanide, ought not, as already stated, to produce a blue precipitate or coloration with ferric chloride.

Uses.—Potassium ferricyanide reacts with solutions of metals in the same manner as potassium ferrocyanide. Of the metallic ferricyanides, the ferrous salt is more particularly characterized by its color, and we therefore apply potassium ferricyanide principally as a test for ferrous compounds.

§ 60.

16. Potassium Sulphocyanide, KCNS.

Preparation.—Mix together 46 parts of anhydrous potassium ferrocyanide, 17 parts of potassium carbonate, and 32 parts of sulphur; introduce the mixture into an iron pan provided with a lid, and fuse over a gentle fire; maintain the same temperature until the swelling of the mass which ensues at first has completely subsided and given place to a state of tranquil and clear fusion; towards the end of the operation, increase the temperature to faint redness, in order to decompose the potassium thiosulphate which has been formed in the process. Pour the mass upon a bright iron plate, break it up, and extract it repeatedly with boiling alcohol of from 80 to 90 per cent. Upon cooling, part of the potassium sulphocyanide separates in colorless crystals; to obtain the remainder, distil the alcohol from the mother-liquor. Dissolve 1 part of the salt in 10 parts of water for use.

Tests and Uses.—Potassium sulphocyanide serves for the detection of ferric compounds, for which it is at once a most characteristic and delicate reagent. It is used further for the detection and separation of copper, which it precipitates as white cuprous sulphocyanide from cupric solutions, upon addition of sulphurous acid. Solution of potassium sulpho-

cyanide must remain colorless when mixed with perfectly pure, dilute hydrochloric acid. It should be neither colored nor precipitated by ammonium sulphide.

b. Salts of the Alkali-earth Metals.

§ 61.

1. Barium Chloride, $BaCl_2.2H_2O$.

Preparation.—a. From heavy-spar. Mix together 8 parts of pulverized barium sulphate, 2 parts of charcoal in powder, and 1 part of common rosin. Put the mixture in a crucible and expose it in a wind-furnace to a long-continued ignition. Triturate the crude barium sulphide obtained, boil about $\frac{9}{10}$ of the powder with 4 times its quantity of water, and add hydrochloric acid until all effervescence of hydrogen sulphide has ceased, and the fluid manifests a slight acid reaction. Add now the remaining $\frac{1}{10}$ of the barium sulphide, boil some time longer, then filter, treat with hydrochloric acid just to acid reaction, heat for a considerable time, filter again, and crystallize. Drain the crystals, redissolve them in water, and crystallize again.

b. From witherite. Pour 10 parts of water upon 1 part of pulverized witherite, and gradually add hydrochloric acid until the witherite is almost completely dissolved. Add a little more finely pulverized witherite, and heat, with frequent stirring, until the fluid has entirely or very nearly lost its acid reaction; add solution of barium sulphide as long as a precipitate forms, and proceed as in *a*. For use, dissolve 1 part of the barium chloride in 10 parts of water.

Tests.—Barium chloride must not alter vegetable colors; its solution must not be colored nor precipitated by hydrogen sulphide (after acidifying with hydrochloric acid), or by ammonium sulphide. Pure sulphuric acid must precipitate all fixed matter from it, so that the fluid filtered from the precipitate formed upon the addition of that reagent leaves not the slightest residue when evaporated in a platinum dish. Potassium chromate should completely precipitate the solution when it has been acidified with a little acetic acid, so that

the liquid, when filtered after standing for two hours in a warm place, remains clear upon the addition of ammonium carbonate. Should a precipitate show itself in making this test (strontium or calcium carbonate), purify the barium chloride by dissolving it in 2 parts of hot water, mixing this solution with twice its volume of alcohol, washing the resulting precipitate with alcohol, and drying it.

Uses.—With many acids, barium forms soluble, with others, insoluble, compounds. This property of barium therefore affords a means of distinguishing the former acids, which are not precipitated by barium chloride, from the latter, in the solution of the salts of which this reagent produces a precipitate. With acids, the precipitated barium salts show varying deportment. By subjecting these salts to the action of acids, we are therefore enabled to subdivide the group of precipitable acids, and even to detect certain individual ones. This renders barium chloride one of the most important reagents for distinguishing between certain groups of acids, but more especially for the detection of sulphuric acid.

§ 62.

2. Barium Nitrate, $Ba(NO_3)_2$.

Preparation.—Treat barium carbonate (either witherite or that precipitated by sodium carbonate from solution of barium sulphide) with dilute nitric acid free from chlorine, and proceed exactly as directed in the preparation of barium chloride from witherite, or else recrystallize the commercial salt. For use, dissolve 1 part of the salt in 15 parts of water.

Tests.—Solution of barium nitrate must not be made turbid by solution of silver nitrate. Other tests are the same as for barium chloride.

Uses.—Barium nitrate is used instead of barium chloride in cases where it is desirable to avoid the presence of a metallic chloride in the fluid.

§ 63.

3. Barium Carbonate, $BaCO_3$.

Preparation.—Dissolve crystallized barium chloride in water, heat to boiling, and add a solution of ammonium carbonate mixed with some caustic ammonia, as long as a precipitate forms. Let the precipitate subside, decant five or six times, transfer the precipitate to a filter, and wash until the washing water is no longer rendered turbid by solution of silver nitrate. Stir the precipitate with water to the consistence of thick milk, and keep this mixture in a stoppered bottle. It must, of course, be shaken every time it is required for use.

Tests.—From the dilute solution in hydrochloric acid (not containing too much free acid), pure sulphuric acid must precipitate all fixed matter. (Compare barium hydroxide, § 37.) Hydrogen sulphide and also ammonium sulphide (after previous addition of ammonia) ought not to color nor precipitate this solution.

Uses.—Barium carbonate decomposes solutions of certain metallic salts, *e.g.*, ferric and aluminium salts, precipitating from them the whole of the metal as hydroxide and basic salt, while some other metallic salts are not precipitated by it. It therefore serves to separate the former from the latter, and affords an excellent means for effecting the separation of ferric oxide and alumina from manganese, zinc, calcium, magnesium, etc. It must be borne in mind, however, that the salts must not be sulphates, as barium carbonate likewise precipitates the latter metals from these compounds.

§ 64.

4. Calcium Sulphate, $CaSO_4.2H_2O$.

Preparation.—Digest and shake powdered, crystallized gypsum (selenite) for some time with water; let the undissolved portion subside, decant, and keep the clear fluid for use.

Uses.—Calcium sulphate, being difficultly soluble, is a con-

venient reagent in cases where it is wished to apply a solution of a calcium salt or of a sulphate of a definite degree of dilution. As dilute solution of a calcium salt, it is used for the detection of oxalic acid; while as dilute solution of a sulphate, it affords an excellent means for distinguishing between barium, strontium, and calcium.

§ 65.

5. Calcium Chloride, $CaCl_2$; *crystallized*, $CaCl_2.6H_2O$.

Preparation.—Dilute 1 part of crude hydrochloric acid with 6 parts of water, and add thereto marble or chalk until the last portion added remains undissolved; now add some slaked lime, then hydrogen sulphide until a filtered portion of the mixture is no longer altered by ammonium sulphide. Then let the mixture stand covered for 12 hours at a gentle heat, filter, exactly neutralize the filtrate, concentrate by evaporation, and crystallize. Let the crystals drain, and dissolve 1 part of the salt in 5 parts of water for use.

Tests.—Solution of calcium chloride must be neutral, and neither be colored nor precipitated by hydrogen sulphide (after acidifying with hydrochloric acid), or by ammonium sulphide or potassium chromate. When mixed with potassium or calcium hydroxide, it must liberate no ammonia. Calcium chloride can be tested for strontium chloride according to § 103.

Uses.—In its action and application, calcium chloride is analogous to barium chloride. As the latter reagent is used to separate the inorganic acids into groups, so calcium chloride serves in the same manner to effect the separation of the organic acids into groups, since it precipitates some of them, while it forms soluble compounds with others. Further, the different conditions under which the various insoluble calcium salts are thrown down enable us to subdivide the group of precipitable acids, as is the case with the barium precipitates.

§ 66.

6. MAGNESIUM SULPHATE, $MgSO_4$; *crystallized*, $MgSO_4.7H_2O$.

Preparation.—Dissolve 1 part of magnesium sulphate of commerce in 10 parts of water. If the salt is not perfectly pure, first subject it to recrystallization.

Tests.—Magnesium sulphate must have a neutral reaction. Its solution, when diluted with an equal quantity of water and mixed with sufficient ammonium chloride, must, after the lapse of half an hour, not appear clouded nor tinged by ammonia, or by ammonium carbonate, oxalate, or sulphide.

Uses.—Magnesium sulphate serves almost exclusively for the detection of phosphoric acid and arsenic acid, which it precipitates from aqueous solutions of phosphates and arsenates, in presence of ammonia and ammonium chloride, in the form of almost absolutely insoluble, highly characteristic salts (ammonium magnesium phosphate or arsenate). Magnesium sulphate is also employed to test ammonium sulphide (see § 41).

c. SALTS OF THE HEAVY METALS.

§ 67.

1. FERROUS SULPHATE, $FeSO_4$; *crystallized*, $FeSO_4.7H_2O$.

Preparation.—Heat an excess of iron nails free from rust, or of clean iron wire, with dilute sulphuric acid until the evolution of hydrogen ceases; filter the sufficiently concentrated solution, add a few drops of dilute sulphuric acid to the filtrate, and allow it to cool. Wash the crystals thus obtained with water very slightly acidulated with sulphuric acid, dry, and keep for use.

Ferrous sulphate can also be very readily prepared from the solution which is obtained in generating hydrogen sulphide by the action of dilute sulphuric acid upon ferrous sulphide.

Tests.—The crystals of ferrous sulphate must have a fine

pale green color. Crystals that have been more or less oxidized by the action of the air, and give a brownish-yellow solution when treated with water, leaving undissolved basic ferric sulphate behind, should be rejected. Hydrogen sulphide must not precipitate solution of ferrous sulphate after addition of some hydrochloric acid, nor even impart a blackish tint to it.

Uses.—Ferrous sulphate has a strong tendency to absorb oxygen, and to be converted into ferric sulphate. It acts therefore as a powerful reducing agent. We employ it principally for the reduction of nitric acid, from which it separates nitric oxide by withdrawing three atoms of oxygen from two molecules of it. In this case, the decomposition of the nitric acid being attended with the formation of a very peculiar brownish-black compound of nitric oxide with an undecomposed portion of the ferrous salt, this reaction affords a particularly characteristic and delicate test for nitric acid. Ferrous sulphate also serves for the detection of ferricyanides, with which it produces a kind of Prussian blue. It is likewise used to effect the precipitation of metallic gold from solutions of that metal.

§ 68.

2. Ferric Chloride, Fe_2Cl_6.

Preparation.—Treat small iron nails in a capacious flask with pure hydrochloric acid of 1.11 sp. gr., using heat towards the end of the operation, until in the presence of an excess of iron no more hydrogen is evolved. Filter the solution into another flask, dilute it with about twice its volume of water, and conduct into it chlorine gas, with frequent shaking, until the fluid no longer produces a blue precipitate in solution of potassium ferricyanide. Heat until the excess of chlorine is expelled. Dilute until the fluid is 20 times the weight of the iron dissolved, and keep for use.

Tests.—Solution of ferric chloride must not contain an excess of acid. This may be readily ascertained by stirring a diluted sample of it with a glass rod dipped in ammonia, when the absence of any excess of acid will be proved by the

formation of a precipitate which fails to dissolve upon agitating the fluid. Potassium ferricyanide must not impart a blue color to it. Hydrogen sulphide must give a white precipitate of sulphur in the diluted solution to which some hydrochloric acid is added. The solution is best tested for arsenic by means of MARSH'S apparatus (see the reactions for arsenious acid in Section III). When evaporated with nitric acid and treated with an abundance of the solution of ammonium molybdate in nitric acid, the solution ought not to give a yellow precipitate even after long standing (phosphoric acid).

Uses.—Ferric chloride serves to subdivide the group of organic acids which calcium chloride fails to precipitate, as it produces precipitates in solutions of benzoates and succinates, but not in cold solutions of acetates and formates. The aqueous solutions of normal ferric acetate and formate exhibit an intensely red color. Ferric chloride is therefore a useful agent for detecting acetic acid, formic acid, and also salicylic acid. It is exceedingly well adapted to effect the decomposition of phosphates of the alkali-earth metals (see phosphoric acid in Section III). It also serves for the detection of ferrocyanides, with which it produces Prussian blue, and, with the co-operation of barium carbonate, for the precipitation of small amounts of phosphoric and of arsenic acids from dilute solutions.

§ 69.

3. SILVER NITRATE, $AgNO_3$.

Dissolve 1 part of the crystallized salt, which may be purchased in a very pure condition, in 20 parts of water.

Tests.—Solution of silver nitrate should have a neutral reaction. Dilute hydrochloric acid must completely precipitate all fixed matter from it. The fluid filtered from the precipitated silver chloride must accordingly leave no residue when evaporated on a watch-glass, and must be neither precipitated nor colored by hydrogen sulphide.

Uses.—With many acids, silver forms soluble, and with others, insoluble compounds. Like barium chloride, silver

nitrate may therefore serve to effect the separation of acids and their arrangement into groups.

Most of the insoluble compounds of silver dissolve in dilute nitric acid, but the chloride, bromide, iodide, and cyanide, ferrocyanide, ferricyanide, sulphocyanide, and sulphide of silver are insoluble in that reagent. Silver nitrate is therefore an excellent agent to distinguish and separate from all others the acids corresponding to the compounds of silver just enumerated. Many of the insoluble silver salts exhibit peculiar colors (silver chromate, silver arsenate), or manifest a characteristic deportment with other reagents or upon the application of heat (silver formate). Silver nitrate is therefore an important agent for the positive detection of certain acids.

§ 70.

4. LEAD ACETATE, $Pb(C_2H_3O_2)_2$; *crystallized*, $Pb(C_2H_3O_2)_2.3H_2O$.

The best lead acetate of commerce is sufficiently pure. For use dissolve 1 part of the salt in 10 parts of water.

Tests.—Lead acetate must completely dissolve in water acidified with a drop or two of acetic acid. The solution must be quite clear and colorless; hydrogen sulphide must throw down all fixed matter from it, so that the filtrate from the lead sulphide is not affected by ammonium sulphide, and leaves no residue upon evaporation. On mixing the solution with ammonium carbonate in excess, and filtering, the filtrate must not show a bluish tint (copper). The solution acidified with nitric acid should not be made cloudy or be precipitated by silver nitrate.

Uses.—With a great many acids, lead forms compounds insoluble in water, which are marked either by peculiarity of color or characteristic deportment. Lead acetate therefore produces precipitates in the solutions of these acids or of their salts, and serves for the detection of several of them. Thus, lead chromate is characterized by its yellow color, lead phosphate by its peculiar deportment before the blowpipe, and lead malate by its ready fusibility.

§ 71.

5. Mercurous Nitrate, $Hg_2(NO_3)_2$, *crystallized*, $Hg_2(NO_3)_2.2H_2O$.

Preparation.—Pour 1 part of pure nitric acid of 1.2 sp. gr. on 1 part of pure mercury in a porcelain dish, and let the vessel stand twenty-four hours in a cool place. Separate the crystals formed from the undissolved mercury and the mother-liquor, and dissolve them in water mixed with $\frac{1}{16}$ part of nitric acid, by trituration in a mortar. Filter the solution and keep the filtrate in a bottle with some metallic mercury covering the bottom.

Tests.—With dilute hydrochloric acid, the solution of mercurous nitrate must give a copious white precipitate of mercurous chloride; hydrogen sulphide must produce no precipitate in the fluid filtered from this, or, at all events, only a trifling black one (mercuric sulphide). This liquid, remaining clear or filtered, must be unchanged by ammonia and ammonium sulphide, and it should give no residue upon evaporation. The solution of mercurous nitrate should contain no free acid. It must therefore give a permanent black precipitate by the addition of even a very small amount of dilute ammonia.

Uses.—Mercurous nitrate acts in a manner analogous to the corresponding silver salt. In the first place, it precipitates many acids, and in the second place, it serves for the detection of several readily oxidizable bodies (*e.g.*, of formic acid), as the oxidation of such bodies, which takes place at the expense of the oxygen of the mercurous salt, is attended with the highly characteristic separation of metallic mercury.

§ 72.

6. Mercuric Chloride, $HgCl_2$.

The corrosive sublimate of commerce is usually sufficiently pure. For use dissolve 1 part of the salt in 16 parts of water.

Uses.—With several acids, *e.g.*, with hydriodic acid, mer-

curic chloride gives peculiarly colored precipitates, and may accordingly be used for the detection of these acids. It is an important agent for the detection of tin, where that metal is in solution in the state of stannous chloride. If only the smallest quantity of the latter compound is present, the addition to the solution of mercuric chloride in excess is followed by separation of mercurous chloride insoluble in water. In a similar manner, mercuric chloride serves also for the detection of formic acid.

§ 73.

7. Cupric Sulphate, $CuSO_4$; *crystallized*, $CuSO_4.5H_2O$.

Preparation.—This reagent may be obtained in a state of great purity from the residue remaining in the flask in the process of preparing hydrogen sodium sulphite (§ 51), by treating with water, applying heat, filtering, adding a few drops of nitric acid, boiling for some time, allowing to crystallize, and purifying the salt by recrystallization. For use dissolve 1 part in 10 parts of water.

Tests.—After precipitation by hydrogen sulphide, ammonia and ammonium sulphide must leave the filtrate unaltered.

Uses.—Copper sulphate is employed in qualitative analysis to effect the precipitation of hydriodic acid in the form of cuprous iodide. For this purpose, it is necessary to mix the solution of 1 part of copper sulphate with $2\frac{1}{2}$ parts of ferrous sulphate, otherwise half of the iodine will separate in the free state. In this process, the ferrous salt changes to ferric salt at the expense of the cupric sulphate, and the latter is thus reduced to a cuprous salt. Copper sulphate is also used for the detection of arsenious and arsenic acids, and likewise serves as a test for the soluble ferrocyanides.

§ 74.

8. Stannous Chloride, $SnCl_2$; *crystallized*, $SnCl_2.2H_2O$.

Preparation.—Reduce grain tin to powder by means of a file, or by fusing it in a small porcelain dish, removing from

the fire, and triturating with a pestle until it has passed again to the solid state. Boil the powder for some time with concentrated hydrochloric acid in a flask (taking care always to have an excess of tin in the vessel) until hydrogen gas is scarcely evolved; dilute the solution with 4 times the quantity of water slightly acidulated with hydrochloric acid, and filter. Keep the filtrate for use in a well-stoppered bottle containing small pieces of metallic tin or some pure tin-foil. If these precautions are neglected, the stannous chloride will soon change to stannic chloride, with separation of white oxychloride, which will render the reagent unfit for use.

Tests.—When added to an excess of solution of mercuric chloride, solution of stannous chloride must immediately produce a white precipitate of mercurous chloride; when treated with hydrogen sulphide, it must give a dark brown precipitate. The liquid filtered from the stannous sulphide ought not to be altered (after previous addition of ammonia) by ammonium sulphide, and should give no residue upon evaporation. Dilute sulphuric acid ought not to cloud or precipitate the stannous chloride solution after it has been diluted with 4 volumes of alcohol (lead). When 1 volume of the stannous chloride solution is heated with about 10 volumes of fuming hydrochloric acid, the liquid should not become brown (arsenic).

Uses.—The great tendency of stannous chloride to absorb oxygen, and thus to form stannic oxide—or rather stannic chloride, as the stannic oxide at the moment of its formation reacts with the free hydrochloric acid present—makes this substance one of our most powerful reducing agents. It is more particularly suited to withdraw part or the whole of the chlorine from chlorides. In the course of analysis, we employ it as a test for mercury; also to effect the detection of gold and arsenic.

§ 75.

9. Hydrochloroplatinic Acid, H_2PtCl_6; *crystallized*, $H_2PtCl_6.6H_2O$.

Preparation.—Treat platinum chips, which have been purified by prolonged heating with concentrated nitric acid, with

concentrated hydrochloric acid and a little nitric acid, in a flask with a narrow neck. Warm gently for a considerable time, and add occasionally more nitric acid until all the platinum is dissolved. Evaporate the solution with repeated additions of hydrochloric acid upon the water-bath, and dissolve the semi-fluid residue in 10 parts of water.

Tests.—Upon evaporation to dryness on the water-bath, hydrochloroplatinic acid must leave a residue which dissolves completely in alcohol. If this solution is evaporated, the residue ignited, treated with warm nitric acid, and the latter is evaporated, no residue, or only a very small one, should be left. The hydrochloroplatinic acid solution should give a pure yellow, not reddish, precipitate with ammonium chloride (iridium).

Uses.—Hydrochloroplatinic acid forms very sparingly soluble salts with potassium and ammonium, but a very soluble salt with sodium. It serves, therefore, for the detection of ammonium and potassium, and for the latter, it is almost the best reagent in the wet way.

§ 76.

10. Sodium Palladious Chloride, Na_2PdCl_4.

Dissolve 5 parts of palladium in nitro-hydrochloric acid, add 6 parts of pure sodium chloride, and evaporate on the water-bath to dryness. The double salt thus obtained must completely dissolve in very little water without leaving a residue of intermixed sodium chloride. Dissolve 1 part of the salt in 12 parts of water for use. The brownish solution affords an excellent means for detecting and separating iodine.

§ 77.

11. Hydrochlorauric Acid, $HAuCl_4$; *crystallized*, $HAuCl_4.3H_2O$.

Preparation.—Take fine cuttings of gold, which may be alloyed with silver or copper, treat them in a flask with nitro-hydrochloric acid in excess, and apply a gentle heat until no more of the metal dissolves, then dilute the solution with 10

parts of water. If the gold was alloyed with copper—which is known by the brownish-red precipitate produced by potassium ferrocyanide in a portion of the solution diluted with water—mix it with solution of ferrous sulphate in excess. This will reduce the hydrochlorauric acid to metallic gold, which will separate in the form of a fine brownish-black powder. Wash the powder in a small flask, and redissolve it in nitro-hydrochloric acid; evaporate the solution on the water-bath, and dissolve the residue in 30 parts of water. If the gold was alloyed with silver, the latter metal remains as chloride upon treating the alloy with nitro-hydrochloric acid. In that case evaporate the solution at once, and dissolve the residue in water for use.

Uses.—Hydrochlorauric acid has a great tendency to yield up its chlorine. It therefore readily converts lower chlorides into higher chlorides, and, with the co-operation of water, lower oxides into higher oxides. These chlorinations or oxidations are usually indicated by the precipitation of pure metallic gold in the form of a brownish-black powder. In the course of analysis, this reagent is used only for the detection of stannous salts, in the solutions of which it produces a brownish-red or purple color or precipitate.

VI. Coloring Matters and Indifferent Vegetable Substances.

§ 78.

1. Test-papers.

α. Blue Litmus-paper.

Preparation.—Digest 1 part of litmus of commerce with 6 parts of water, and filter the solution; divide the intensely blue filtrate into 2 equal parts; saturate the free alkali in one part, by repeatedly stirring with a glass rod dipped in very dilute sulphuric acid, until the color of the fluid just appears red; add now the other part of the blue filtrate, pour the whole fluid into a dish, and draw strips of filter-paper through it; suspend these strips upon strings and leave them

to dry. The color of litmus-paper must be uniform, and neither too light nor too dark. It must be easily wet by aqueous liquids.*

Uses.—The red coloring matters contained in commercial litmus, in its aqueous extract, and in the papers colored with it, appear blue only on account of the presence of alkaline bases. If one of the blue preparations comes in contact with free acid, this combines with the bases, and, in consequence, the proper red color of the coloring matters of litmus appears. Litmus-paper affords, therefore, an excellent means for detecting free acids. Weak, volatile acids are capable of only transiently combining with the bases occasioning the blue coloration; consequently the blue color appears again upon their volatilization. It must be borne in mind, however, that many soluble, normal salts of the heavy metals also effect the change of the blue color to red.

β. Reddened Litmus-paper.

Preparation.—Stir blue solution of litmus with a glass rod dipped in dilute sulphuric acid, and repeat this process until the fluid has just turned distinctly red. Soak strips of paper in the solution, and dry them as in α. The dried strips must look distinctly red.

Uses.—Free alkalies and alkali-earths, and also the sulphides of their metals, give a blue color to red litmus-paper; alkali carbonates and the soluble salts of several other weak acids, especially of boric acid, possess the same property. This reagent therefore serves for the detection of these bodies in general. Ammonia changes the color of red litmus-paper to blue only temporarily, for upon the volatilization of the ammonia, the red color appears again.

γ. Turmeric-paper.

Preparation.—Extract bruised turmeric-root with cold water, in order to remove a yellow coloring matter, which

* The litmus-paper prepared according to the above directions fully suffices for the purposes of qualitative analysis. In regard to more refined methods of preparation, see Zeitschr. f. analyt. Chem., **7**, 466; **12**, 368; **21**, 992; **28**, 697.

has little delicacy towards alkalies. Dry the residue, digest 1 part of it with 6 parts of alcohol, and soak strips of fine, unglazed paper in the filtered tincture. The dried turmeric-paper must have a fine yellow color, and be easily wet by aqueous liquids.

Uses.—Like red litmus-paper, turmeric-paper serves for the detection of free alkalies, etc., which change its yellow color to brown. It is not so delicate a test as the other reagent papers, but the change of color is highly characteristic, and is very distinctly perceptible in many *colored* fluids; we cannot well dispense, therefore, with this paper. When testing with turmeric-paper, it must be borne in mind that, besides the substances enumerated in *β*, several other bodies (boric acid, for instance) possess the property of turning its yellow color to red (especially upon drying). It thus affords an excellent means for the detection of boric acid.

All test-papers are cut into strips, which must be kept in well-closed boxes or in black bottles, since they are bleached by the continued action of light.

§ 79.

2. Solution of Indigo.

Preparation.—Take from 4 to 6 parts of fuming sulphuric acid, add slowly, and in small portions at a time, 1 part of finely pulverized indigo, taking care to keep the mixture well stirred. The acid has at first imparted to it a brownish tint by the matter which the indigo contains in admixture, but it subsequently turns deep blue. Elevation of temperature to any considerable extent must be avoided, as part of the indigo is thereby destroyed. When dissolving large quantities of the substance, it is therefore advisable to place the vessel in cold water. When the whole of the indigo has been added to the acid, cover the vessel, let it stand forty-eight hours, then pour its contents into 20 times the quantity of water, mix, filter, and keep the filtrate for use.

B. REAGENTS IN THE DRY WAY.

I. Fluxes and Decomposing Agents.

§ 80.

1. Mixture of Sodium Carbonate and Potassium Carbonate, $Na_2CO_3 + K_2CO_3$.

Preparation.—Digest for a few hours 10 parts of powdered, purified cream of tartar with 10 parts of water and 1 part of hydrochloric acid, with frequent stirring, upon the water-bath. Transfer the mass to a funnel provided with a small filter in the apex, let it drain, cover it with a double disk of thick paper which is turned up around the edge, and wash by pouring repeatedly small quantities of cold water upon this paper, until, after the addition of nitric acid, the washings are no longer clouded by silver nitrate solution; dry the hydrogen potassium tartrate thus freed from calcium (and phosphoric acid). Prepare also some pure potassium nitrate by dissolving the commercial salt in half its weight of water at the boiling temperature, filtering the solution into a porcelain or stoneware dish by means of a filter contained in a warmed porcelain funnel, and stirring it diligently with a porcelain or wooden spatula until cold. Bring the crystalline powder upon a funnel which is loosely stopped with cotton, let it drain, press it down firmly, make the surface level, cover it with a double disk of slowly permeable paper turned up around the edge, and pour water upon this in small portions and at proper intervals of time until the wash-water which comes away is no longer made turbid by silver nitrate. Then transfer the contents of the funnel to a porcelain dish, dry the salt, and pulverize it finely.

Mix 2 parts of the pure cream of tartar with 1 part of the pure saltpeter. Put the fully dried mixture in portions into an iron pot which has been brightly scoured and heated to low redness. After deflagration has taken place, heat it strongly, until a test taken out gives an entirely color-

less solution with water. Pulverize the carbonized mass with water, filter, wash somewhat, and evaporate the solution in a porcelain—or, better, in a silver—dish until it becomes covered with a permanent crust of salt. Let it now cool with constant stirring, bring the crystals of potassium carbonate upon a funnel, let them drain well, and wash a little. Dry the substance completely, best in a platinum or silver dish, and preserve in well-closed vessels. Upon evaporation, the mother-liquor yields a preparation containing traces of alumina and silicic acid, which is serviceable for many purposes.

Pure potassium carbonate can also be obtained without difficulty from commercial potassium bicarbonate. Pulverize this, wash it with small amounts of cold water until, after acidifying with nitric acid, the washings are no longer clouded by silver nitrate and barium nitrate; dry the powder and convert it by heating (best in a platinum or silver dish) into normal potassium carbonate.

Mix intimately 13 parts of the pure potassium carbonate with 10 parts of pure anhydrous sodium carbonate, and preserve the mixture in well-closed bottles. This mixture can be directly prepared by deflagrating 20 parts of pure acid potassium tartrate with 9 parts of pure sodium nitrate, and evaporating the solution, obtained as described above, to dryness; or also by igniting pure sodium potassium tartrate (Rochelle salt), extracting the carbonaceous mass with water, and evaporating the colorless solution to dryness.

The salt should be tested like sodium carbonate (§ 49). The presence of any potassium cyanide is detected by adding some ferrous-ferric solution and then an excess of hydrochloric acid, when a bluish-green coloration is produced, and a blue precipitate which settles after long standing.

Uses.—If silicic oxide or a silicate is fused with about 4 parts (consequently with an excess) of potassium or sodium carbonate, carbon dioxide escapes with effervescence, and an alkali silicate is formed, which, being soluble in water, may be separated from such metallic oxides as may remain undissolved; from the solution, hydrochloric acid separates the silicic acid. If sodium or potassium carbonate is fused together with sulphates of barium, strontium, or calcium,

there are formed carbonates of the alkali-earth metals and sodium or potassium sulphate, which are compounds that can be separated by water, and in which new compounds, both the base and the acid of the originally insoluble salt may now be readily detected. Instead of potassium carbonate or sodium carbonate alone, we use preferably the mixture considered above, for fluxing insoluble silicates and sulphates, because it has a lower melting-point than either of its constituents, and thus renders it possible to flux the compounds under consideration by the use of a simple gas-lamp or of BERZELIUS'S alcohol-lamp. The fusion with alkali carbonates is invariably effected in a platinum crucible, provided no reducible metallic compound is present.

§ 81.

2. BARIUM HYDROXIDE, $Ba(OH)_2$.

Preparation.—Heat the barium hydroxide crystals, obtained according to § 37, in a silver or platinum dish at a gentle heat until all the water of crystallization is driven off, pulverize the remaining white mass, and keep it for use in well-stoppered bottles.

Uses.—Barium hydroxide fuses at a low red heat without losing its water. If silicates which are undecomposable by acids are fused with about 4 times their weight of this reagent, basic silicates are formed which are decomposable by acids. If the fused mass, therefore, is treated with water and hydrochloric acid, the solution evaporated to dryness, and the residue digested with dilute hydrochloric acid, the silicic acid remains undissolved, while the metallic chlorides go into solution. Use is made of barium hydroxide for fluxing when it is desired to test silicates for alkalies. It is deservedly preferred to barium carbonate or nitrate, which may be used for the same purpose, because it does not require a very high temperature like the first, and does not occasion spattering on account of evolved gas like the latter. Fluxing with barium hydroxide is done in a silver or platinum crucible.

§ 82.

3. Calcium Fluoride, CaF_2, and other Fluorides.

Select the purest fluor-spar possible, especially such as is free from alkalies, pulverize it finely, and keep for use.

Uses.—When used together with sulphuric acid, calcium fluoride serves for decomposing silicates which are insoluble in acids, and especially for detecting the alkali metals contained in them. If aqueous *hydrofluoric acid* which is pure (leaving no residue when evaporated in a platinum dish) is available (this can now to be purchased in wax bottles) or pure *ammonium fluoride* or *hydrogen ammonium fluoride*, these are to be preferred to calcium fluoride for decomposing silicates. (Compare *silicic acid*, § 180.) Hydrogen ammonium fluoride, $HF.NH_4F$, can be quickly prepared by strongly supersaturating hydrofluoric acid or hydrofluosilicic acid with ammonia. After warming gently, filter if necessary, best with the employment of a funnel of gutta-percha or hard rubber, and evaporate the filtrate in a platinum dish to dryness. The preparation must volatilize without leaving a residue when heated in a platinum dish (the commercial salt sometimes contains lead). It is best prepared directly for use, because it can be kept only in platinum vessels, or in those of gutta-percha or hard rubber, and it is inclined to deliquesce. The solution of this salt, supersaturated with ammonia, serves also for the recognition and separation of lithium.

§ 83.

4. Sodium Nitrate, $NaNO_3$.

Preparation.—Exactly neutralize pure nitric acid with pure sodium carbonate, and evaporate to crystallization; dry the crystals thoroughly, triturate, and keep the powder for use.

Tests.—A solution of sodium nitrate must not be made turbid by solution of silver nitrate or barium nitrate, nor precipitated by sodium carbonate.

Uses.—Sodium nitrate serves as a very powerful oxidizing

agent, by yielding oxygen to combustible substances when heated with them. We use this reagent principally to convert several metallic sulphides, more particularly the sulphides of tin, antimony, and arsenic, into oxides or acids; also to effect the rapid and complete combustion of organic substances. For the latter purpose, however, *ammonium nitrate* is sometimes preferable, and is prepared by neutralizing nitric acid with ammonium carbonate.

§ 84.

5. Potassium Disulphate, $K_2S_2O_7$.

Preparation.—Mix in a platinum dish or a large platinum crucible 87 parts of neutral potassium sulphate with 49 parts of pure concentrated sulphuric acid, heat to low redness until the mass is uniformly liquid and perfectly clear, then pour it into a platinum dish standing in cold water, or upon a fragment of porcelain or something of the kind; break it up, and preserve it for use.

Tests.—The potassium disulphate must dissolve in water with ease to a clear fluid with a strong acid reaction. The solution must not be rendered turbid nor precipitated by hydrogen sulphide or by ammonia and ammonium sulphide.

Uses.—At the temperature of fusion, potassium disulphate dissolves and decomposes many bodies which cannot be dissolved and decomposed without considerable difficulty, at least, by acids in the wet way, such as ignited alumina, titanic oxide, chrome ironstone, etc. This reagent, therefore, is of service in effecting the solution or decomposition of such bodies. The fusion is preferably effected in platinum vessels.

II. Blowpipe Reagents.

§ 85.

1. Sodium Carbonate, Na_2CO_3.

Preparation.—See § 49.

Uses.—Sodium carbonate serves, in the first place, to promote the reduction of oxidized substances in the inner flame

of the blowpipe. In fusing, it brings the oxides into the most intimate contact with the charcoal support, and enables the flame to embrace every part of the substance under examination. With salts of the heavy metals, the reduction is preceded by separation of the base. In this process, it also co-operates chemically by the transposition of its constituents (according to R. WAGNER, in consequence of the formation of sodium cyanide). Where the quantity operated upon is very minute, the reduced metal is often found in the pores of the charcoal. In such cases, the parts surrounding the cavity which contained the substance are dug out with a knife, triturated in a small mortar, and the charcoal is then washed off from the metallic particles, which now become visible either in the form of powder or as small, flattened spangles, as the case may be.

Sodium carbonate serves, in the second place, as a solvent, and platinum wire is the most convenient support for testing the solubility of substances in the fused reagent. Only a few of the bases dissolve in fusing sodium carbonate, but acids dissolve in it with facility. It is also applied as a decomposing agent and a flux, more particularly to effect the decomposition of the insoluble sulphates, with which it exchanges acids, the newly formed sodium sulphate being reduced in the inner flame to sodium sulphide. It is further employed to effect the decomposition of arsenious sulphide, with which it forms a double arsenious and sodium sulphide, and sodium arsenite or arsenate, thus converting it to a state which permits its subsequent reduction by hydrogen. In the dry way, sodium carbonate is also the most sensitive reagent for the detection of manganese, as when fused in the outer flame with a substance containing manganese it produces a green, opaque bead, owing to the formation of sodium manganate.

§ 86.

2. POTASSIUM CYANIDE, KCN.

Preparation.—See § 57.

Uses.—Potassium cyanide is an exceedingly powerful reducing agent in the dry way, excelling in its action almost

all other reagents, and separating the metals not only from most oxygen compounds, but also from many sulphur compounds. In the former case, this reduction is attended with formation of potassium cyanate by the absorption of oxygen, and in the latter case, with formation of potassium sulphocyanide by the taking up of sulphur. By means of this reagent, we may effect the reduction of metals from their compounds with the greatest facility (usually even in a porcelain crucible over a simple gas or alcohol flame). We may, for instance, produce metallic antimony from antimonious acid or from antimony sulphide, metallic iron from ferric oxide, etc. The readiness with which potassium cyanide enters into fusion greatly facilitates the reduction of the metals. It is a most valuable and important agent for effecting the reduction of stannic oxide, antimonic acid, and particularly of arsenious sulphide. It is equally important as a blowpipe reagent, its action being exceedingly energetic, and substances like stannic oxide, the reduction of which by means of sodium carbonate requires a tolerably strong flame, are reduced by potassium cyanide with the greatest facility. In blowpipe experiments, we invariably use a mixture of equal parts of sodium carbonate and potassium cyanide, the admixture of the former being intended here to check in some measure the excessive fusibility of the latter. This mixture, besides being a far more powerful reducing agent than the simple sodium carbonate, has, moreover, this great advantage, that it is absorbed by the pores of the charcoal with extreme facility, and thus permits the production of the metallic globules in a state of the greatest purity.

§ 87.

3. Sodium Formate, $NaCHO_2$.

Preparation.—Heat in a tubulated retort connected with a condenser and a receiver 200 parts of glycerine and 12 parts of crystallized oxalic acid. At 75° a lively reaction begins, and at 90° it is in full operation. It consists in the decomposition of oxalic acid into carbonic and formic acids:

$H_2C_2O_4 = CO_2 + HCHO_2$. The glycerine induces the reaction, but remains unchanged as far as the final result is concerned. Aqueous formic acid goes over with the liberated carbon dioxide. As soon as the evolution of carbon dioxide has almost ceased, add 12 parts more of oxalic acid. The liquid now going over is richer in formic acid than the first distillate. After the reaction has almost stopped, add 13 parts of oxalic acid, and afterwards again 13 parts. In this way, 130 parts of distillate are obtained, which contains about 56 per cent of formic acid (BERTHELOT, LORIN). Neutralize this with sodium hydroxide which is free from sulphate, evaporate the solution to dryness, dry the residue at 130°, and preserve the anhydrous salt thus obtained in a well-closed bottle.

Tests.—Sodium formate is, above all, to be tested to find if it contains any sulphate. Its aqueous solution ought, therefore, to give no turbidity with barium chloride after the addition of a few drops of hydrochloric acid.

Uses.—Sodium formate is a powerfully acting reducing agent, and can often be used instead of the poisonous potassium cyanide. Its action depends upon the fact that it goes over into sodium carbonate by heating, with the liberation of hydrogen and carbon monoxide (F. NELISSEN).

§ 88.

4. SODIUM TETRABORATE (BORAX), $Na_2B_4O_7$; *crystallized*, $Na_2B_4O_7.10H_2O$.

The purity of commercial borax may be tested by adding to its solution sodium carbonate, or, after previous addition of nitric acid, solution of barium nitrate and of silver nitrate. The borax may be considered pure if these reagents fail to produce any alteration in the solution; but if either of them causes the formation of a precipitate, or renders the fluid turbid, recrystallization is necessary. The pure crystallized borax is exposed to a gentle heat in a platinum crucible until it ceases to swell. It is then left to cool, and afterwards pulverized and kept for use.

Uses.—Boric acid shows a great affinity for oxides when it comes in contact with them in a molten condition. In the first place, therefore, it combines directly with oxides; in the second place, it expels weaker acids from their salts; and in the third place, it facilitates the oxidation of metals, and of sulphur and halogen compounds in the outer blowpipe flame, owing to the fact that it dissolves the resulting oxides. The borates which form are usually fusible themselves, but they fuse far more readily together with sodium borate, the latter acting simply as a flux or forming double salts. In sodium tetraborate, we have, first, active boric acid; second, sodium borate; and, consequently, both conditions combined, whereby, as stated, oxides, sulphides, metals, etc., are brought into a state of solution and fusion. For these reasons, borax is of the greatest importance as a blowpipe reagent. In the process of fusing with borax, platinum wire is usually selected for a support. The loop of the wire is moistened or heated to redness, then dipped into the powder, and exposed to the outer flame, a colorless bead of fused borax being thus produced. A small portion of the substance is then attached to the bead, by bringing the latter into contact with it while still hot or by having previously moistened it. The bead with the substance adhering is next exposed to the gas or blowpipe flame, and the reactions are observed. The following points ought to be more particularly watched: (1) Whether the substance dissolves to a transparent bead, and retains its transparency on cooling; (2) whether the bead exhibits a distinct color, which in many cases at once clearly indicates the individual metal contained in the substance, as is the case, for instance, with cobalt; and (3) whether the bead manifests the same or a different deportment in the outer and in the inner flame. Reactions of the last kind arise from the reduction of higher to lower oxides, or even to the metallic state, and are for some substances particularly characteristic.

§ 89.

5. HYDROGEN SODIUM AMMONIUM PHOSPHATE, $HNaNH_4PO_4.8H_2O$. (*Microcosmic Salt, Salt of Phosphorus.*)

Preparation.—*a.* Heat to boiling 6 parts of hydrogen disodium phosphate and 1 part of pure ammonium chloride with 2 parts of water, and let the solution cool. Free the resulting crystals from the sodium chloride which adheres to them, by recrystallization, with addition of some solution of ammonia. Dry the purified crystals, pulverize, and keep for use.

b. Take 2 equal parts of pure orthophosphoric acid, and add solution of soda to one and solution of ammonia to the other, until both fluids have a distinct alkaline reaction; mix the two together, and let the mixture crystallize.

Tests.—Hydrogen sodium ammonium phosphate dissolves in water to a fluid with feebly alkaline reaction. The yellow precipitate produced in this fluid by silver nitrate must completely dissolve in nitric acid. Upon fusion on a platinum wire, microcosmic salt must give a clear and colorless bead.

Uses.—On heating hydrogen sodium ammonium phosphate, two molecules of it give up a molecule of water and two molecules of ammonia, together with the water of crystallization, leaving hydrogen sodium pyrophosphate, $H_2Na_2P_2O_7$; upon heating more strongly, an additional molecule of water escapes, and two molecules of readily fusible *sodium metaphosphate*, $NaPO_3$, are left behind. The action of sodium metaphosphate is quite analogous to that of sodium tetraborate. However, in some cases we prefer it to borax as a solvent or flux, the beads which it forms with many substances being more distinctly colored than those of borax. Platinum wire is also used for a support in the process of fluxing with sodium metaphosphate. The loop must be made small and narrow, otherwise the bead will not adhere to it. The operation is conducted as directed for borax.

§ 90.

6. COBALT NITRATE, $Co(NO_3)_2$; *crystallized*, $Co(NO_3)_2.6H_2O$.

Preparation.—Dissolve commercial cobalt oxide in hydrochloric acid, evaporate the solution to dryness upon the

water-bath, take up the residue with water, add precipitated barium carbonate suspended in water, in some excess, let it stand for several hours with frequent stirring, filter, and wash; add to the filtrate more barium carbonate, pass in chlorine, let it stand for some time with frequent agitation, separate the precipitate consisting of cobaltic hydroxide and the excess of barium carbonate from the solution containing the nickel, wash, dissolve in hydrochloric acid, precipitate the barium by adding sulphuric acid in only slight excess, and then, without previously filtering, pass in hydrogen sulphide while the liquid is heated to about 70°. Filter, add ammonia to alkaline reaction, then ammonium sulphide until this predominates; finally, add acetic acid to distinctly acid reaction. Filter off the cobalt sulphide, wash it, dissolve it in aqua regia, evaporate off the excess of acid, take up with water, and precipitate hot with sodium carbonate. After washing the precipitate, mix it while still moist with an excess of oxalic acid. Wash the rose-red cobalt oxalate well, dry it, and ignite it in a glass tube in a stream of hydrogen. It decomposes in this operation into carbon dioxide, which escapes, and metallic cobalt. Wash the latter first with water containing acetic acid, then with pure water; dissolve it in dilute nitric acid, evaporate the solution on the water-bath to dryness, and dissolve 1 part of the residue in 10 parts of water.

Tests.—Solution of cobalt nitrate must be free from other metals, especially from salts of the alkali metals; and when precipitated with ammonium sulphide and filtered, the filtrate upon evaporation on platinum must leave no fixed residue. Treated with potassium cyanide in excess and bromine, with the addition, if necessary, of sodium hydroxide, there should form no black precipitate of nickelic hydroxide, even after about an hour.

Uses.—Upon ignition with certain infusible bodies (zinc oxide, alumina), cobalt monoxide forms peculiarly colored compounds, and may accordingly serve for their detection (see Section III).

SECTION III.

REACTIONS, OR DEPORTMENT OF BODIES WITH REAGENTS.

§ 91.

In my introductory remarks, I stated that the operations and experiments of qualitative analysis have for their object the conversion of the unknown constituents of any given compound into forms of which we know the deportment, relations, and properties, and which will accordingly permit us to draw correct inferences regarding the several constituents of which the analyzed compound consists. The greater or less value of such analytical experiments, like that of all other inquiries and investigations, depends upon the greater or less degree of certainty with which they lead to definite results, whether of a positive or negative nature. But as a question does not render us any wiser if the language is unknown in which the answer is returned, so in like manner will analytical investigations prove unavailing if we do not understand the mode of expression in which the desired information is conveyed to us; in other words, if we do not know how to interpret the phenomena produced by the action of reagents upon the substance examined.

Therefore, before we can undertake the practical investigation of analytical chemistry, it is indispensable that we should possess the most accurate knowledge of the deportment, relations, and properties of the new forms into which we intend to convert the substances we wish to analyze. Now this knowledge consists, in the first place, in a clear conception and comprehension of the conditions necessary for the formation of the new compounds and the manifestation of the various reactions; and in the second place, in

a distinct impression of the color, form, and physical properties which characterize such compounds. This section of the work demands, therefore, not only the most careful and attentive study, but requires that the student should verify the facts by experiment.

In the present work, those substances which are in many respects analogous are arranged in groups, since by comparing their analogies with their differences, the latter are placed in the clearest possible light.

A.—Deportment of the Metallic, mostly Basic, Radicals.

§ 92.

Before proceeding to the special study of the several metals, I give here a general view of all of them classified in groups, showing which belong to each group. The basis for this classification will appear in connection with the special consideration of each group.

First group:

Potassium, sodium, ammonium (cæsium, rubidium, lithium).

Second group:

Barium, strontium, calcium, magnesium.

Third group:

Aluminium, chromium (beryllium, thorium, zirconium, yttrium, cerium, lanthanum, didymium, titanium, tantalum, niobium).

Fourth group:

Zinc, manganese, nickel, cobalt, iron (uranium, thallium, indium, gallium, vanadium).

Fifth group:

Silver, mercury, lead, bismuth, copper, cadmium (palladium, rhodium, osmium, ruthenium).

Sixth group:

Gold, platinum, tin, antimony, arsenic (germanium, iridium, molybdenum, tungsten, tellurium, selenium).

Of these metals, only those printed in italics are found distributed extensively and in large quantities in that portion of the earth's crust which is accessible to investigation. There-

fore, these are most important in chemistry, the arts and manufactures, agriculture, pharmacy, etc., and will be dwelt upon at greater length. The remainder are more briefly considered in paragraphs printed in smaller type, which may be passed over when the study of analytical chemistry is first taken up. The metals which are still the subject of scientific discussion, especially those imperfectly known, such as erbium, terbium, davyum, scandium, holmium, ytterbium, samarium, philippium, decipium, thulium, etc., are not considered in this book. The properties and reactions of the metals themselves I have given only in the case of those that are more frequently met with in the metallic state.

§ 93.

FIRST GROUP.

More common metals: POTASSIUM, SODIUM, AMMONIUM.

Rarer metals: CÆSIUM, RUBIDIUM, LITHIUM.

Properties of the Group.—The hydroxides of the metals of the first group—the alkalies—are readily soluble in water, as are also the sulphides, carbonates, and phosphates of these metals. (Lithium carbonate and phosphate, however, dissolve with difficulty.) Accordingly, the alkalies do not precipitate one another, nor do the alkali carbonates or phosphates (in the case of lithium, a high degree of dilution of the solutions is presupposed), nor are they precipitated by hydrogen sulphide under any conditions. The solutions of the hydroxides, as well as of the sulphides and carbonates of this group, restore the blue color of reddened litmus-paper, and impart an intensely brown tint to turmeric-paper.

Special Reactions of the More Common Metals of the First Group.

§ 94.

a. POTASSIUM, K. (*Oxide*, K_2O.)

1. POTASSIUM HYDROXIDE and POTASSIUM SALTS are not volatile at a faint *red heat*. The hydroxide deliquesces in the

air, and the oily liquid formed absorbs carbon dioxide rapidly, but without solidifying.

2. Nearly all the POTASSIUM SALTS are soluble in water. Those with colorless acids are colorless. The normal salts of strong acids do not alter vegetable colors. Potassium carbonate crystallizes (in combination with water of crystallization) with difficulty, and deliquesces in the air; while potassium sulphate is anhydrous, and suffers no alteration upon exposure.

3. In the neutral and acid solutions of potassium salts, *hydrochloroplatinic acid* produces a yellow, crystalline, heavy precipitate of POTASSIUM PLATINIC CHLORIDE, K_2PtCl_6. In concentrated solutions, this precipitate separates immediately upon the addition of the reagent; but in dilute solutions, it forms only after some time, often after a *considerable* time. Very dilute solutions are not precipitated by the reagent. The precipitate consists of octahedrons discernible under the microscope. Alkaline solutions must be acidified with hydrochloric acid before the hydrochloroplatinic acid is added. The precipitate is difficultly soluble in water, and the presence of free acids does not greatly increase its solubility. It is insoluble in alcohol. Hydrochloroplatinic acid is therefore a particularly delicate test for potassium salts dissolved in alcohol. The best method of applying this reagent is to evaporate the aqueous solution of the potassium salt with hydrochloroplatinic acid nearly to dryness on the water-bath, and to pour a little water over the residue (or, better still, some alcohol, provided no substances insoluble in that menstruum are present), when the potassium platinic chloride will be left undissolved. Care must be taken not to confound this salt with ammonium platinic chloride, which greatly resembles it (see § 96, 5).

4. In neutral or alkaline solutions, *tartaric acid* produces a white, quickly subsiding, *granular* crystalline precipitate of HYDROGEN POTASSIUM TARTRATE, $HKC_4H_4O_6$. (To alkaline solutions, the reagent must be added until the fluid shows a strongly acid reaction.) In concentrated solutions, this precipitate separates immediately, but in dilute solutions, often only after the lapse of *considerable* time. Vigorous shaking or stirring of the fluid greatly promotes its formation. Very

dilute solutions are not precipitated by this reagent. Free alkalies and free mineral acids dissolve the precipitate. It is sparingly soluble in cold, but pretty readily soluble in hot water. In acid solutions, the free acid must, if practicable, first be expelled by evaporation and ignition, or the solution must be neutralized with sodium hydroxide or carbonate.

Hydrogen sodium tartrate answers still better than free tartaric acid as a test for potassium. The reaction is the same in kind, but different in degree, being more delicate with the salt than with the free acid. Where the former is used, the sodium salt of the acid that was combined with the potassium is formed, whereas when free tartaric acid is the test applied, the acid originally combined with the potassium is liberated. This action tends to increase the dissolving power of the water present upon the hydrogen potassium tartrate, and thus to check the separation of the latter: $KNO_3 + HNaC_4H_4O_6 = HKC_4H_4O_6 + NaNO_3$.

5. If five or six drops of *cobalt nitrate solution* (§ 90) and about 1 cc of acetic acid are added to about 2 cc of a 10 per cent solution of *sodium nitrite*, a deep orange-yellow fluid having a strong odor of nitrous acid is obtained. When added to the neutral solution of a potassium salt until the color becomes yellow, this freshly prepared reagent produces a yellow, crystalline precipitate of POTASSIUM COBALTIC NITRITE, $K_3Co(NO_2)_6$. In concentrated solutions, this takes place immediately, but in more dilute ones, only after some time. 1 part of potassium chloride dissolved in 1000 parts of water will still give the reaction (DE KONINCK). Alkaline solutions should be acidified with acetic acid before the test is made. Acid solutions should be neutralized with sodium carbonate, if the acid cannot be removed by evaporation. The properties of the precipitate are given under § 125, 14. Ammonium salts give a similar reaction, but only in concentrated solutions. The salts of the alkaline-earth metals are not precipitated by this reagent.

6. If a potassium salt which is volatile at an intense red heat is held on the loop of a fine platinum wire in the fusing zone of the BUNSEN *gas-lamp* (p. 31), the salt volatilizes, and imparts a BLUISH-VIOLET tint to the part of the flame above the sample. Potassium chloride and potassium nitrate volatilize

rapidly, the carbonate and sulphate less rapidly, and the phosphate still more slowly; but all distinctly show the reaction, though in decreasing degree. If it is wished to obtain a more uniform manifestation of the reaction, *i.e.*, a manifestation independent of the nature of the acid that may chance to be combined with the potassium, the sample may be simply moistened with sulphuric acid, dried at the border of the flame, and then introduced into the fusing zone. With silicates and other potassium compounds of difficult volatility, the reaction may be insured by first fusing the sample with pure gypsum, as this serves to form calcium silicate and potassium sulphate, and the latter salt readily colors the flame. Decrepitating salts are ignited in a platinum spoon before they are attached to the loop. The sample of potassium salt may also be held before the apex of the inner *blowpipe flame* produced with a spirit-lamp. The presence of a sodium salt completely obscures the potassium coloration of the flame.

If the potassium flame is observed through the *indigo prism* (p. 38), the coloration appears sky-blue, violet, and at last intensely crimson, even through the thickest layers of the solution. Admixtures of calcium, sodium, and lithium compounds do not alter this reaction, as the yellow rays cannot penetrate the indigo solution, and the rays of the lithium flame are able to pass through the thinner layers of the solution, but not through the thicker layers. The exact spot where the penetrating power of the rays of the lithium flame ceases has to be marked by the operator on his indigo prism. But organic substances which impart luminosity to the flame might lead to mistakes, and must therefore, if present, first be destroyed by heat. Instead of the indigo prism, one containing potassium permanganate (p. 38) can be used, or also a blue glass. In the presence of lithium, sufficiently thick layers of the absorbing media should be used, so that the red of the lithium cannot penetrate them.

The spectrum of the potassium flame produced by the *spectroscope* (p. 40) is mapped on Plate I. It contains two characteristic lines—the red line α and the indigo-blue line β.

7. If a potassium salt (potassium chloride is best) is heated with a little water, *alcohol* (burning with a colorless flame)

added, and the liquid heated and kindled, the flame appears VIOLET. The reaction is far less delicate than the one mentioned in 6, and the presence of sodium hides it completely.

§ 95.

b. SODIUM, Na. (*Oxide*, Na_2O.)

1. SODIUM HYDROXIDE and SODIUM SALTS present in general the same properties and reactions as potassium and its corresponding compounds. The oily fluid which sodium hydroxide forms by deliquescing in the air resolidifies speedily by absorption of carbon dioxide. Sodium carbonate crystallizes readily, and the crystals, $Na_2CO_3.10H_2O$, effloresce rapidly when exposed to the air. The same applies to the crystals of sodium sulphate, $Na_2SO_4.10H_2O$. Sodium chloride is much less soluble in concentrated hydrochloric acid than in water.

2. If a sufficiently concentrated solution of a sodium salt with neutral or alkaline reaction is mixed (conveniently in a watch-glass) with a solution of *acid potassium pyroantimonate* prepared according to the directions of § 54, the mixture remains clear at first, or appears only slightly turbid. However, upon rubbing with a glass rod the part of the glass wet by the fluid, a crystalline precipitate of SODIUM PYROANTIMONATE, $H_2Na_2Sb_2O_7.6H_2O$, speedily separates, which first makes its appearance along the lines rubbed with the rod, and subsides from the fluid as a heavy, sandy precipitate. From dilute solutions of sodium salts, the precipitate separates only after some time, *e.g.*, twelve hours. From very dilute solutions, it does not separate at all. The precipitated sodium pyroantimonate is *invariably* crystalline. Where it has separated slowly, it occasionally consists of well-formed, microscopic, tetragonal octahedrons, but more frequently of four-sided prisms, terminated by pyramids. Where it has separated promptly, it appears in the form of small boat-shaped crystals. Presence of large quantities of potassium salts interferes very considerably with the reaction. Acid solutions cannot be tested with potassium pyroantimonate, as, from the latter substance, free acids will separate pyroantimonic acid. Before adding the reagent, it is indispensable,

therefore, to remove, if possible, the free acid by evaporation or ignition, or where this is not practicable, by neutralizing the acid solution with a little potassium carbonate until the reaction is feebly alkaline. It should also be borne in mind that only those solutions which contain no salts other than those of sodium, potassium, and perhaps ammonium, can be tested with potassium pyroantimonate.

3. If sodium salts are held in the fusing zone of the BUNSEN *gas-lamp* or in the inner *alcohol blowpipe flame*, they show, with regard to their relative volatility and the action of decomposing agents upon them, a similar deportment to the salts of potassium. The sodium salts are, however, a little less volatile than the corresponding potassium salts. But the most characteristic sign of the presence of sodium salts is the INTENSE YELLOW COLORATION which they impart to the flame. This reaction will effect the detection of the minutest quantities of sodium, and is not obscured by the presence of large quantities of potassium salts.

It is characteristic of the sodium flame that a crystal of potassium dichromate appears colorless in its light, and that a slip of paper coated with mercuric iodide appears white, with a faint shade of yellow (BUNSEN); also that the flame looks orange-yellow when observed through a *green glass* (MERZ). These reactions are not obscured by presence of salts of potassium, lithium, and calcium.

The spectrum (Plate I) shows only a single yellow line α in an ordinary *spectroscope*, but with a very powerful apparatus, two lines will be distinctly visible, although they are exceedingly close to each other. The reaction is so delicate that the sodium chloride contained in atmospheric dust generally suffices to give a sodium spectrum, although a faint one.

4. If a SODIUM SALT (sodium chloride is the best) is treated as has been given for potassium under 7, the *alcohol flame* is colored STRONGLY YELLOW. This reaction, also, is not obscured by the presence of potassium salts.

5. *Hydrochloroplatinic acid* produces no precipitate in neutral or acid solutions of sodium salts. Sodium platinic chloride dissolves readily both in water and in alcohol, and it crystallizes in long, yellow prisms.

6. *Tartaric acid* and *hydrogen sodium tartrate* fail to precipitate even concentrated, neutral solutions of sodium salts.

§ 96.

AMMONIUM, NH_4.

1. AMMONIA, NH_3, is gaseous at the common temperature; but is most frequently dealt with in its aqueous solution, in which it betrays its presence at once by its penetrating odor. It is expelled from this solution by the application of heat. It may be assumed that the solution contains ammonium oxide, $(NH_4)_2O$, or hydroxide, NH_4OH (see § 36).

2. All AMMONIUM SALTS are volatile at a *low heat*, either with or without decomposition. Most of them are readily soluble in water. The solutions are colorless if the acid exerts no coloring influence. The normal compounds of ammonium with strong acids do not alter vegetable colors.

3. If AMMONIUM SALTS are triturated together with *slaked lime* (best with the addition of a few drops of water), or, either in the solid state or in solution, are heated with solution of potassium or sodium hydroxide, ammonia is liberated in the gaseous state, and betrays its presence—1, by its characteristic ODOR; 2, by its REACTION with moistened test-papers; and 3, by giving rise to the formation of WHITE FUMES when any object (*e.g.*, a glass rod) moistened with hydrochloric acid, nitric acid, acetic acid, or any of the volatile acids, is brought in contact with it. These fumes arise from the formation of solid ammonium salts produced by the contact of the gases in the air. Hydrochloric acid is the most delicate test in this respect, but acetic acid admits less readily of a mistake. If the expulsion of the ammonia is effected in a small beaker, best with slaked lime, with addition of a very little water, and the beaker is covered with a watch-glass having a strip of moistened turmeric- or reddened litmus-paper attached to the center of the convex side, the reaction will show the presence of even *very* minute quantities of ammonia. In such cases, however, the reaction is not immediate, but requires some time for its manifestation. It is promoted and accelerated by the application of a gentle heat.

4. If a solution of *normal mercurous nitrate* is added to a solution which contains free ammonia or ammonium carbonate, a black precipitate results, which in very dilute solutions is at first whitish-gray. Therefore, if the ammonia evolved according to 3, being set free in a test-tube, is allowed to act upon a glass rod which is moistened with mercurous nitrate and introduced, or, being liberated in a beaker, is allowed to act upon a drop of mercurous nitrate solution spread upon the convex side of a watch-glass covering it, or upon a strip of paper under the watch-glass, moistened with this solution, the moistened part of the rod, the drop, or the paper, becomes colored from gray to black. This manner of producing the reaction is to be especially recommended, because considerable amounts of salts present in the liquid to be tested may retard the reaction or prevent it. The precipitate which forms in this reaction, the so-called mercurius solubilis HAHNEMANNI, is not always of the same composition. The precipitate first formed at a great degree of dilution, which produces the compound in the purest condition, corresponds to the formula $NH_2Hg_2NO_3$ (LÖSCH). The formation is illustrated by the following equation: $Hg_2(NO_3)_2+2NH_3 = NH_2Hg_2NO_3+NH_4NO_3$.

5. *Hydrochloroplatinic acid* shows the same deportment with ammonium salts as with salts of potassium. Like the corresponding potassium compound, the yellow precipitate of AMMONIUM PLATINIC CHLORIDE, $(NH_4)_2PtCl_6$, consists of octahedrons discernible under the microscope.

6. From highly concentrated solutions with neutral reaction, *tartaric acid* throws down after some time part of the ammonium as HYDROGEN AMMONIUM TARTRATE, $HNH_4C_4H_4O_6$. Less concentrated solutions are not precipitated. *Hydrogen sodium tartrate* precipitates concentrated solutions much more completely, and produces a precipitate even in more dilute solutions. The precipitate is white and crystalline. Its separation may be promoted by shaking, or rubbing the glass inside with a glass rod. By solvents it is acted upon like the corresponding potassium salt, except that it is a little more readily soluble in water and in acids.

§ 97.

Recapitulation and Remarks.—The potassium and sodium salts are not volatile at a moderate red heat, while the ammonium salts volatilize readily, and may therefore be easily separated from the former by ignition. The expulsion of *ammonia* by slaked lime affords the surest means of ascertaining the presence of ammonium salts. In case of doubt, the reaction which ammonia gives with mercurous nitrate is more decisive than the alkaline reaction of the gas, for the vapors of the volatile alkaloids, such as coniine and nicotine, give an alkaline reaction, while they give to the mercurous nitrate solution a whitish or yellowish-gray turbidity, but do not blacken it.

Potassium salts can be detected by the aid of hydrochloroplatinic acid and of tartaric acid or hydrogen sodium tartrate only after the removal of the ammonium salts which may be present, because both give exactly similar reactions with these reagents. Even in testing for potassium salts with sodium nitrite and cobalt solution, the removal of any accompanying ammonium salts is to be recommended. After the removal of the ammonium compounds, *potassium* is clearly and positively characterized by any one of these three reagents. The reactions will show with certainty only in concentrated fluids, and dilute solutions must therefore first be greatly concentrated. A single drop of a *concentrated* solution will give a positive result, which cannot be obtained with a large quantity of a dilute fluid. Potassium is most simply detected in potassium platinic chloride and in acid potassium tartrate by first decomposing these salts by gentle ignition. From the platinum compound, the decomposition of which is facilitated by the addition of some oxalic acid, the potassium is obtained as chloride, while potassium carbonate is obtained from the acid tartrate. When heated with sulphuric acid, potassium cobaltic nitrite yields potassium sulphate and cobalt sulphate. For the direct detection of potassium in potassium iodide, tartaric acid or acid sodium tartrate is better suited than hydrochloroplatinic acid or sodium nitrate and cobalt solution, since upon the addition of the first, the separation of the potassium platinic

chloride is somewhat obscured by the formation of a deep, dark red liquid, containing platinic iodide and some free iodine; while in the second case, nitrous acid and potassium iodide react, with the separation of iodine.

Sodium can be recognized with complete certainty in the wet way with acid sodium pyroantimonate, if the reagent has been properly prepared; if the solution of the sodium salt is concentrated, neutral, or feebly alkaline, and is free from interfering bases; and if it is noticed once for all that sodium pyroantimonate always separates in a crystalline condition and never in a flocculent state. If there is occasion to detect in this way small quantities of sodium in the presence of much potassium, the latter is first separated by hydrochloroplatinic acid, the platinum is removed from the filtrate by means of hydrogen sulphide and filtration, the solution is evaporated to dryness, gently ignited, taken up in very little water, and then tested with acid potassium pyroantimonate.

Potassium and sodium can be detected by flame coloration much more easily and more quickly, and also with far greater delicacy, than in the wet way. We have seen, indeed, that the sodium coloration completely obscures that of potassium, even when only a small amount of a sodium salt is present with a large quantity of a potassium salt; but if the spectroscope is made use of, the spectra of both appear so clearly and beautifully that no error is possible. The presence of sodium chloride actually increases the strength of the potassium lines up to a proportion of 100 parts of sodium chloride to 1 part of potassium chloride, but with greater proportions of sodium chloride, the delicacy of the spectroscopic detection of potassium again decreases (GOOCH and HART). Where a spectroscope is not available, the potassium coloration can be distinctly recognized in a flame colored strongly yellow by sodium, by means of a glass prism filled with a solution of indigo or of potassium permanganate, or by the use of a blue glass; while the sodium coloration can be more accurately tested, if necessary, by the use of mercuric iodide paper, or of a green glass, in the manner already described.*

* Concerning the detection of very small amounts of potassium and sodium by the microscopic observation of crystallized potassium and sodium compounds, compare HAUSHOFER'S "Mikroskopische Reactionen," pp. 55 and 98; BEHRENS, Zeitschr. f. analyt. Chem., 30, 134 and 135; FREY, *ibid.*, 32, 204.

The following methods serve for the detection of *ammonium in exceedingly minute quantities*, as, for instance, in natural waters; they depend upon the separation of certain mercury compounds which are insoluble in water, and which contain the nitrogen or the nitrogen and part of the hydrogen of the ammonia:

a. If water containing a trace of ammonia or ammonium carbonate is mixed with a few drops of solution of mercuric chloride, a white precipitate is formed, even in a very dilute solution. The precipitate consists of mercurammonium chloride, NH_2HgCl, thus: $2NH_3 + HgCl_2 = NH_2HgCl + NH_4Cl$. If the solution is extraordinarily dilute, no turbidity occurs, but on the addition of a few drops of solution of sodium carbonate, the fluid will become turbid or opalescent in a few minutes, even after *very extensive dilution.* This reaction takes place when water containing a trace of a neutral ammonium salt is mixed with a few drops of solution of mercuric chloride and a few drops of solution of sodium carbonate. The precipitate which separates on the addition of sodium carbonate consists of one molecule of the previously mentioned precipitate with one molecule of mercuric oxide: $2NH_3 + 4HgCl_2 + 3K_2CO_3 = 2(NH_2HgCl + HgO) + H_2O + 6KCl + 3CO_2$. Too much mercuric chloride and sodium carbonate must not be added, otherwise a yellow precipitate of mercuric oxychloride would be formed (BOHLIG, SCHÖYEN).

b. Upon adding to a solution of potassium mercuric iodide containing potassium hydroxide,* a little of a fluid containing ammonia or an ammonium salt, a reddish-brown precipitate is formed if the ammonia is present in some quantity; but there is always a yellow coloration produced, at least after some time, even if only *most minute* traces of ammonia are present. The precipitate consists of dimercurammonium iodide, $NHg_2I.H_2O$, and the reaction

* This (NESSLER'S reagent) is prepared by heating to boiling, with stirring, 35 g of potassium iodide and 13 g of mercuric chloride with 800 cc of water. When a clear solution results, a cold saturated solution of mercuric chloride is added drop by drop until a permanent precipitate just begins to form. Then 160 g of potassium hydroxide or 120 g of sodium hydroxide are added, the volume is brought to 1 liter by addition of water, a little more mercuric chloride solution is added, and the liquid is allowed to become clear by settling. The solution has a very pale, yellowish color.

is as follows: $2(2KI.HgI_2) + NH_3 + 3KHO = NHg_2I.H_2O + 7KI + 2H_2O$. Application of heat promotes the separation of the precipitate. Presence of chlorides of the alkali metals, or of their salts with oxygen acids, does not interfere with the reaction; but presence of alkali-metal cyanides and sulphides, as well as free carbonic acid and alkali-metal acid carbonates, will prevent it (J. NESSLER). In the presence of the latter, potassium or sodium hydroxide is therefore to be added. If bicarbonates or any other soluble salts of the alkali-earth metals are present, these are precipitated from the solution by the addition of an exactly sufficient quantity of a freshly boiled and subsequently cooled solution containing about 1 part of sodium hydroxide to 2 parts of sodium carbonate. The precipitate is allowed to settle in a closed cylinder, and the decanted, clear solution is tested with NESSLER'S reagent.

For the recognition of small amounts of ammonia by the *microscopic method*, an appropriate means is offered by the production and testing of ammonium magnesium phosphate crystals (see HAUSHOFER, p. 13; BEHRENS, Zeitschr. f. analyt. Chem., **30**, 166).

§ 98.

Special Reactions of the Rarer Metals of the First Group.

1. CÆSIUM, Cs; 2. RUBIDIUM, Rb.

The cæsium and rubidium compounds, especially the latter, occur rather widely disseminated in nature, but in very minute quantities only. They have hitherto been found chiefly in the mother-liquors of mineral waters, and in a few minerals (lepidolite, carnallite, etc.). Cæsium has also been found in considerable quantities in pollux, and traces of rubidium have been detected in beet-molasses and in the ashes of plants. In general, the cæsium and rubidium compounds bear great resemblance to those of potassium, more particularly in this, that their aqueous solutions, even when moderately concentrated, are precipitated by *hydrochloroplatinic acid*, and also that those compounds that are volatile at a red heat tinge the *flame* violet. The most notable characteristic differences, on the other hand, are that the precipitates produced by hydrochloroplatinic acid are far more insoluble in water than potassium platinic chloride. At 10°, 100 g of water will dissolve 900 mg of potassium platinic chloride, but only 154 mg of the rubidium platinic chloride, and as little as 50 mg of the cæsium platinic chloride. Again, the alums show great differences as

regards their solubility in cold water. Thus, 100 parts of water at 17° dissolve 13.5 parts of potassium alum, 2.27 parts of rubidium alum, and .619 parts of cæsium alum. Moreover, the flames colored by cæsium and rubidium compounds give *spectra* quite different from the potassium spectrum (see Plate I). The cæsium spectrum is especially characterized by the two blue lines α and β, which are remarkable for their wonderful intensity and sharp outline; also by the line γ, which, however, is less strongly marked. In the rubidium spectrum, the splendid indigo-blue lines marked α and β strike the eye by their extreme brilliancy. Less brilliant, but still very characteristic, are the lines δ and γ. To detect both alkalies in presence of each other by the spectroscope, the chlorides and not the carbonates should be taken, since with the latter salts, the rubidium spectrum is not always distinct in the presence of that of cæsium (ALLEN, HEINTZ). It should also be mentioned that cæsium carbonate is soluble in absolute alcohol, while rubidium carbonate is insoluble in that liquid. Still, a separation of the two metals is effected only with difficulty by this means, as they seem to form a double salt which is not absolutely insoluble in alcohol. It is more easy to separate them when they are in the form of acid tartrates, for the hydrogen rubidium tartrate dissolves in 8.5 parts of boiling water and 84.57 parts of water at 25°, while the corresponding salt of cæsium dissolves in 1.02 parts of boiling water and 10.32 parts of water at 25° (ALLEN). (Hydrogen potassium tartrate requires 15 parts of boiling water and 89 parts of water at 25°.)

The following methods are recommended as the most reliable ones for separating cæsium from rubidium as well as from potassium: (*a*) Add stannic chloride to the hot, concentrated solution containing a rather large amount of strong hydrochloric acid, filter the precipitate of cæsium stannic chloride upon a hardened filter, wash it with concentrated hydrochloric acid, dissolve it in boiling water containing some hydrochloric acid, precipitate with concentrated hydrochloric acid, filter again, and wash with concentrated hydrochloric acid. The filtrate contains the rubidium, also any potassium that was present, as well as stannic chloride. Any ammonium present, however, is found in the precipitate as ammonium stannic chloride, and ammonium salts are, therefore, to be previously removed (F. STOLBA). (*b*) Add a solution of antimonious chloride in strong hydrochloric acid to the concentrated solution of the salt, filter the precipitate of cæsium antimonious chloride, $3CsCl.2SbCl_3$, which separates immediately, upon a hardened filter, and wash it with strong hydrochloric acid. All the other alkali metals, as well as ammonium, are not precipitated, and are found with antimony trichloride in the filtrate (GODEFFROY).

Concerning the microscopic detection of cæsium and rubidium, compare HAUSHOFER, p. 31; and BEHRENS, Zeitschr. f. analyt. Chem., 30, 137.

3. Lithium, Li.

Lithium is found rather widely disseminated in nature, but not in large quantities. It is often met with in the analysis of mineral waters and ashes of plants, less frequently in the analysis of minerals, and only rarely in that of technical and pharmaceutical products. Lithium forms the transition from the first to the second group of metals. Its hydroxide dissolves with difficulty in water, and it does not attract moisture from the air. Most of its salts are soluble in water, while some of them are deliquescent (lithium chloride). Lithium carbonate is difficultly soluble, particularly in cold water. It is more soluble in water containing carbonic acid. Upon boiling, *hydrogen sodium phosphate* produces in not too dilute solutions of salts of lithium, a white, crystalline precipitate of lithium phosphate, $2Li_3PO_4.H_2O$, which quickly subsides to the bottom of the vessel. This reaction, which is characteristic of lithium, is rendered much more delicate by adding with the sodium phosphate a little sodium hydroxide solution, just sufficient to leave the reaction alkaline, evaporating the mixture to dryness, treating the residue with a little water, and adding an equal volume of ammonia solution. By this course, even very minute quantities of lithium will be separated as $2Li_3PO_4.H_2O$. The precipitate fuses before the blowpipe, upon fusion with sodium carbonate gives a clear bead, and when fused upon charcoal, it is absorbed by the pores of the latter. It dissolves in hydrochloric acid to a fluid which, when diluted and supersaturated with ammonia, remains clear in the cold, but upon boiling gives a heavy, crystalline precipitate of the compound mentioned above. (Reactions by which the lithium phosphate differs from the phosphates of the alkali-earth metals.) If pure *ammonium fluoride* (free from ammonium silicofluoride) is added to a not too dilute solution of a lithium salt, together with an excess of ammonium hydroxide, a white, gelatinous precipitate of lithium fluoride gradually separates. Since potassium, rubidium, and cæsium fluorides are easily soluble in water, even when it is ammoniacal, and since sodium fluoride requires only 70 parts of a mixture of equal parts of ammonia solution and water to dissolve it, while lithium fluoride requires 3500 parts of the same for its solution, it is evident that lithium can be separated from the other alkali metals in the form of lithium fluoride, especially if the amount of sodium salts present is not too great. Very small amounts of lithium are best separated by evaporating the solution of alkali salts, after adding ammonium fluoride, to dryness in a platinum dish upon the water-bath, and treating the residue with dilute ammonia solution (A. Carnot).* [If several volumes of amyl alcohol are added to a very concentrated solution of the chlorides of lithium, sodium, and potassium, best after making slightly acid with hydrochloric acid, and the whole is boiled until the water has disappeared, and the boiling is then continued until about one

* Zeitschr. f. analyt. Chem., **29**, 332.

half of the remaining amyl alcohol has been removed in order that the remainder may become anhydrous, the lithium chloride, being very soluble in the liquid, may be separated from the almost absolutely insoluble sodium and potassium chlorides by filtering the hot liquid through a dry filter (GOOCH).]

Tartaric acid and *hydrochloroplatinic acid* fail to precipitate even concentrated solutions of lithium salts. If salts of lithium are exposed to the *gas* or *blowpipe flame*, in the manner described for potassium (§ 94, 6), they tinge the flames carmine-red. Silicates containing lithium require addition of gypsum to produce this reaction, or, better still, gypsum and pure fluorspar in the proportion 2 : 1. Lithium phosphate will tinge the flame carmine-red if the fused bead is moistened with hydrochloric acid. The sodium coloration conceals that of lithium. In presence of sodium, therefore, the lithium tint must be viewed through a blue glass, or through a thin layer of indigo solution. Presence of a small proportion of potassium will not conceal the lithium coloration. In presence of a large proportion of potassium, the lithium may be detected by placing the substance in the fusing zone, viewing the colored flame through the indigo prism, and comparing it with a pure potassium flame produced in the opposite part of the fusing zone. Viewed through thin layers, the lithium colored flame now appears redder than the pure potassium flame; viewed through somewhat thicker layers, the flames appear at last equally red, if the proportion of the lithium to the potassium is only trifling; but when lithium predominates in the sample examined, the intensity of the red coloration imparted by lithium decreases perceptibly when viewed through thicker layers, while the pure potassium flame is scarcely impaired thereby. By this means, lithium may be detected in potassium salts, even though present only in the proportion of one part in several thousand parts of the latter. Unless present in very large quantities, sodium interferes but little with these reactions (CARTMELL. BUNSEN).

The *lithium spectrum* (Plate I) is most brilliantly characterized by the splendid carmine-red line α and the very faint, orange-yellow line β. The flame of a BUNSEN burner yields only these two lines, but if lithium chloride is introduced into a hydrogen flame, a dull blue line is perceptible, which becomes brilliant if the oxyhydrogen flame is used. Its position nearly coincides with the weaker of the two blue lines of cæsium (TYNDALL, FRANKLAND). If alcohol is poured over lithium chloride and then ignited, the flame also shows a carmine-red tint. Presence of sodium salts will mask this reaction.

Concerning the detection of lithium by microchemical methods, compare HAUSHOFER, p. 89; and BEHRENS, Zeitschr. f. analyt. Chem., 30, 136.

To detect small quantities of cæsium, rubidium, and lithium, in presence of very large quantities of sodium or potassium, as is necessary, for example, in the analysis of mineral waters, extract the dry chlorides, with addition of a few drops of hydrochloric acid, with alcohol of 90 per cent,

which leaves behind the far larger portion of the sodium and potassium chlorides. Evaporate the solution to dryness, dissolve the residue in very little water, and precipitate with hydrochloroplatinic acid. Filter off the precipitate, boil it repeatedly with small quantities of water to remove the potassium platinic chloride present, and in the course of this process examine repeatedly by the spectroscope. For this purpose place a slight amount of the precipitate upon a small piece of moistened filter-paper, wind a very fine platinum wire about the folded paper, carbonize it at the top of the flame, avoiding too high a temperature, and then place the sample in the fusing zone of the flame, which is in front of the slit of the spectroscope. The potassium spectrum will now be found to grow fainter and fainter, while the spectra of rubidium and cæsium will become visible, if these metals are present. Evaporate to dryness the fluid filtered from the platinum precipitate, with the addition of some oxalic acid, ignite the residue gently to decompose the sodium platinic chloride and the excess of hydrochloroplatinic acid, moisten with hydrochloric acid, drive off the acid again, and finally extract the lithium chloride with a mixture of absolute alcohol and ether. The evaporation of the solution obtained leaves the lithium chloride behind in a state of almost perfect purity, and it may then be further examined and tested. Before concluding from the simple coloration of the flame, that lithium is present, it is advisable, in order to guard against the chance of error, to test a portion of the residue, dissolved in water, with sulphuric acid and alcohol, to make sure that strontium or calcium is not present. The addition of hydrochloric acid, which is repeatedly prescribed in the above process to precede the extraction of the lithium chloride with alcohol, is necessary, for the reason that lithium chloride, even by moderate ignition, is converted by the action of aqueous vapor into lithium hydroxide, which then attracts carbonic acid, forming lithium carbonate, which is insoluble in alcohol. Lithium chloride can be separated from considerable amounts of sodium and potassium chlorides by adding fuming hydrochloric acid to the concentrated solution of the salts, and pouring off the solution containing lithium chloride and small amounts of the other chlorides from the separated potassium and sodium chlorides.

§ 99.

SECOND GROUP.

Barium, Strontium, Calcium, Magnesium.

Properties of the Group.—The oxides of the metals of this group, the alkali earths, unite with water to form hydroxides which are more or less soluble in that liquid. Magnesium oxide and hydroxide, however, dissolve but very sparingly in water. The solutions manifest alkaline reaction, which in the

case of magnesia is most clearly apparent when that earth is laid upon moistened test-paper. The neutral carbonates and phosphates of the alkali-earth metals are insoluble in water. The solutions of their salts are therefore precipitated, even in dilute solution, by carbonates and phosphates of the alkali metals. This property distinguishes the metals of the second group from those of the first. From the metals of the following groups, they are distinguished by the solutions being precipitated neither by hydrogen sulphide nor by ammonium sulphide. The alkali earths and the salts of their metals are white or colorless (if the acid radical of the salt does not impart a color to it), and not volatile at a moderate red heat. The solutions of the nitrates and chlorides of this group are not precipitated by barium carbonate.

Special Reactions.

§ 100.

a. BARIUM, Ba. (*Oxide*, BaO.)

1. BARIUM HYDROXIDE, $Ba(OH)_2$, is readily soluble in hot water, but rather sparingly so in cold water. It dissolves freely in dilute hydrochloric or nitric acid. It fuses at a red heat without losing water, but upon stronger ignition the water is lost (BRÜGELMANN).

2. Most of the BARIUM SALTS are insoluble in water. The soluble salts do not affect vegetable colors, and with the exception of chloride, bromide, and iodide of barium, are decomposed upon ignition in a glass tube. The insoluble salts dissolve in dilute hydrochloric acid, except barium sulphate and barium silicofluoride. BARIUM CHLORIDE and NITRATE are almost insoluble in alcohol, insoluble in a mixture of equal parts of absolute alcohol and ether, and do not deliquesce in the air. Concentrated solutions of barium salts are precipitated by hydrochloric or nitric acid added in large proportions, as barium choride and nitrate are not soluble in the concentrated aqueous solutions of these acids.

3. *Ammonia* produces no precipitate in aqueous solutions of barium salts. From highly concentrated solutions only,

potassium or sodium hydroxide (free from carbonic acid) precipitate crystals of BARIUM HYDROXIDE, $Ba(OH)_2.8H_2O$, which redissolve in water.

4. *Soluble carbonates* throw down BARIUM CARBONATE, $BaCO_3$, in the form of a white precipitate. If the solution was previously acid, complete precipitation takes place only upon heating the fluid. In ammonium chloride, the precipitate is soluble to a trifling, yet clearly perceptible, extent, and therefore ammonium carbonate produces no precipitate in very dilute barium solutions containing much ammonium chloride.

5. *Sulphuric acid* and all the soluble *sulphates*, more particularly solution of *calcium sulphate*, produce, even in very dilute solutions, a heavy, finely pulverulent, white precipitate of BARIUM SULPHATE, $BaSO_4$. This is generally formed immediately upon the addition of the reagent, but from highly dilute solutions, especially when strongly acid, it separates only after some time. The precipitate is insoluble in alkalies, nearly so in dilute acids, but perceptibly soluble in concentrated hydrochloric and nitric acids, especially upon heating, as well as in concentrated solutions of ammonium, potassium, sodium, calcium, and magnesium salts. The solvent action of the acids and also of the salts is counteracted, or at least very much diminished, if sulphuric acid or a sulphate is present in considerable excess. Rather large quantities of calcium chloride may completely prevent the precipitation of small amounts of barium by means of calcium sulphate (LÜDEKING *).

6. *Hydrofluosilicic acid* throws down BARIUM SILICOFLUORIDE, $BaSiF_6$, in the form of a colorless, crystalline, quickly subsiding precipitate. In dilute solutions, this precipitate is formed only after the lapse of some time. Very dilute solutions are not precipitated, for barium silicofluoride is not entirely insoluble in water. With the addition of an equal volume of alcohol, the precipitation takes place quickly, and so completely that the filtrate remains clear upon the addition of sulphuric acid. Hydrochloric and nitric acids and ammonium salts increase its solubility in water as well as in alcohol.

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* Zeitschr. f. analyt. Chem., 29, 556.

7. In neutral or alkaline solutions, *sodium phosphate* produces a white precipitate of HYDROGEN BARIUM PHOSPHATE, $HBaPO_4$, which is soluble in free acids. Addition of ammonia only slightly increases the quantity of this precipitate, a portion of which is converted into barium phosphate, $Ba_3(PO_4)_2$, in this process. Ammonium chloride dissolves the precipitate to a clearly perceptible extent.

8. In moderately dilute solutions, *ammonium oxalate* produces a white, pulverulent precipitate of BARIUM OXALATE, $BaC_2O_4.H_2O$, which is soluble in hydrochloric and nitric acids. When recently thrown down, this precipitate also dissolves in oxalic and acetic acids, but the solutions speedily deposit acid barium oxalate, $H_2Ba(C_2O_4)_2.2H_2O$, in the form of a crystalline powder.

9. *Potassium chromate* and *dichromate* produce a bright yellow precipitate of barium chromate, $BaCrO_4$, even in very dilute solutions of barium salts. This is very difficultly soluble in cold water, somewhat more readily in boiling water, while ammonium salts increase its solubility very noticeably. But all these conditions of solubility are completely changed when potassium chromate is added in excess in making the precipitation, so that in the case of acid solutions, no free acid is present, but in the place of this, potassium dichromate is formed. Under these conditions, the precipitation of barium is complete. Hydrochloric or nitric acid dissolves barium chromate, and ammonia precipitates it again from the reddish-yellow solution.

10. Soluble barium salts, when triturated and heated with dilute *alcohol*, give to its flame a GREENISH-YELLOW COLOR.

11. If barium salts are held on the loop of a platinum wire in the fusing zone of the BUNSEN *gas flame*, the part of the flame above the sample is colored YELLOWISH-GREEN; or if the barium salts are held in the inner (alcohol) *blowpipe flame*, the same coloration is imparted to the part of the flame beyond the sample. With the soluble barium salts, and also with barium carbonate and sulphate, the reaction is immediate or takes place very soon. The phosphate, however, requires previous moistening of the sample with sulphuric or hydrochloric acid, by which means barium may be detected by the flame coloration in silicates decomposable by acids.

Silicates which hydrochloric acid fails to decompose must be fused with sodium carbonate, when the barium carbonate produced will show the reaction. It is characteristic of the yellowish-green barium coloration of the flame that it appears bluish-green when viewed through the green glass. If the sulphates are used for the experiment, presence of calcium and strontium will not interfere with the reaction. The barium *spectrum* is shown in Plate I. The green lines α and β are the most intense; γ is less marked, but still characteristic. Since platinum wire sometimes contains barium (KRAUT), it is well to find first whether it will give a barium spectrum by itself.

12. Barium sulphate is not, or, more correctly, scarcely at all, decomposed by cold solutions of the *bicarbonates of the alkali metals* or of *ammonium carbonate*. It behaves in the same way with a boiling solution of 1 *part of potassium carbonate and* 3 *parts of potassium sulphate*, but its behavior towards all these reagents is essentially different when strontium sulphate or calcium sulphate is mixed with it (see p. 162). Repeated action of boiling solution of sodium or potassium carbonate upon barium sulphate succeeds in the end in completely decomposing that salt. Barium sulphate is readily decomposed by fusion with sodium carbonate, with the formation of sodium sulphate, which is soluble in water, and of barium carbonate, insoluble in that liquid.

§ 101.

b. STRONTIUM, Sr. (*Oxide*, SrO.)

1. STRONTIUM HYDROXIDE and the STRONTIUM SALTS have nearly the same general properties and reactions as the corresponding barium compounds. Strontium hydroxide is more sparingly soluble in water than barium hydroxide, and it loses its water only upon strong ignition. STRONTIUM CHLORIDE dissolves in *absolute alcohol* and deliquesces in moist air. STRONTIUM NITRATE is almost insoluble in *absolute alcohol*, and is insoluble in a mixture of equal volumes of *absolute alcohol and ether*. Strontium nitrate does not deliquesce in the air.

2. With *ammonia, potassium hydroxide, sodium hydroxide,* also with the *alkali carbonates,* and with *sodium phosphate,* the strontium salts show nearly the same reactions as the barium salts. In ammonium chloride, strontium carbonate dissolves to a less marked degree than barium carbonate.

3. *Sulphuric acids and sulphates* throw down STRONTIUM SULPHATE, $SrSO_4$, in the form of a white precipitate. When thrown down from concentrated solutions, it is at first flocculent and amorphous, afterwards pulverulent and crystalline; but from dilute solutions, it is immediately pulverulent and crystalline. Application of heat promotes the precipitation. Strontium sulphate is less insoluble in water than barium sulphate; hence it separates from rather dilute solutions only after some time. *Calcium sulphate* solution causes no immediate precipitation except in very concentrated, and especially in hot, strontium solutions; yet it precipitates more dilute solutions after some time. Potassium, sodium, calcium, and magnesium salts increase the solubility of strontium sulphate, so that, for example, strontium cannot be precipitated by calcium sulphate solution in the presence of much calcium chloride (LÜDEKING). In hydrochloric and nitric acids, strontium sulphate dissolves perceptibly. Presence of large quantities of these acids will accordingly most seriously impair the delicacy of the reaction. An excess of sulphuric acid tends to counteract the solvent action of acids and salts. Strontium sulphate is insoluble in alcohol, so that the addition of the latter promotes its precipitation very greatly. Strontium sulphate does not dissolve in a concentrated solution of ammonium sulphate, even by boiling, but if mixed with calcium sulphate, it dissolves with the latter to a marked degree in this reagent.

4. *Hydrofluosilicic acid* fails to produce a precipitate, even in rather concentrated solutions of strontium salts, because strontium SILICOFLUORIDE, $SrSiF_6$, is moderately soluble in cold water. Hot water dissolves it somewhat less easily. It dissolves in small amount in dilute alcohol, but the stronger the alcohol the less readily it dissolves. Hydrochloric acid greatly increases the solubility of the salt in water, and also in alcohol, but to a somewhat less degree.

5. Even from rather dilute solutions, *ammonium oxalate*

precipitates STRONTIUM OXALATE, $2SrC_2O_4.5H_2O$, in the form of a white powder, which dissolves readily in hydrochloric and nitric acids, and perceptibly in ammonium salts, but is only sparingly soluble in oxalic and acetic acids.

6. *Potassium dichromate* does not precipitate solutions of salts of strontium, even when they are concentrated. *Potassium chromate* at first produces no precipitate, but on long standing, if the solution is neutral and not very dilute, bright yellow STRONTIUM CHROMATE, $SrCrO_4$, is precipitated in a crystalline condition. This does not take place, however, in solutions acidified with acetic acid. The precipitate dissolves rather difficultly in pure water, more abundantly in water containing acetic acid or ammonium salts, but hydrochloric, nitric, and chromic acids dissolve it easily. None of these solutions are precipitated by the addition of potassium chromate in excess. Alcohol does not dissolve strontium chromate, and even dilute alcohol scarcely dissolves it at all. Neutral solutions of strontium salts to which potassium chromate is added are therefore precipitated by the addition of even small amounts of alcohol. Warming to 70° facilitates the precipitation.

7. If strontium salts which are soluble in water or alcohol are heated with dilute *alcohol*, and the latter is ignited, they impart to the flame, especially upon stirring, an intense CARMINE-RED COLOR.

8. If a strontium salt is held in the fusing zone of the BUNSEN *gas flame*, or in the inner *alcohol blowpipe flame*, an INTENSELY RED COLOR is imparted to the flame. The reaction is most distinct with strontium chloride, less clear with the hydroxide and carbonate, fainter still with the sulphate, and scarcely appears with strontium salts of fixed acids. Therefore, after its first exposure to the flame, the sample is moistened with hydrochloric acid, and again thus exposed. If strontium sulphate is likely to be present, the sample is first exposed a short time to the reducing flame (to produce strontium sulphide), before it is moistened with hydrochloric acid. Viewed through the *blue glass*, the strontium flame appears purple or rose (difference between strontium and calcium, the latter showing a faint greenish-gray color when treated in this manner). This reaction also is most clearly

apparent if the sample is moistened with hydrochloric acid when brought into the flame. In presence of barium, the strontium reaction shows only upon the first introduction into the flame of the sample moistened with hydrochloric acid. The strontium *spectrum* is shown in Plate I. It contains a number of characteristic lines, more especially the orange line α, the red lines β and γ, and the blue line δ, the latter being more particularly suited for the detection of strontium in presence of barium and calcium.

9. Strontium sulphate is completely decomposed by digestion with solution of sodium or potassium carbonate. It is also decomposed even by digestion with solutions of *ammonium carbonate* or of *alkali-metal bicarbonates*, but much more rapidly by boiling with a solution of 1 part of *potassium carbonate and* 3 *parts of potassium sulphate.* Its decomposition by ammonium carbonate, by the alkaline bicarbonates, and also by potassium carbonate and sulphate is, however, not complete when it is mixed with barium sulphate; for in presence of the latter, a certain amount of strontium sulphate always remains undecomposed.

§ 102.

c. CALCIUM, Ca. (*Oxide, Lime,* CaO.)

1. CALCIUM OXIDE (quicklime), CALCIUM HYDROXIDE (slaked lime), and CALCIUM SALTS, in their general properties and reactions, present a great similarity to the corresponding barium and strontium compounds. Calcium hydroxide is far more difficultly soluble in water than the barium and strontium hydroxides, and dissolves more sparingly in hot than in cold water. Calcium hydroxide loses its water upon ignition. CALCIUM CHLORIDE and NITRATE are soluble in *absolute alcohol*, and also in a mixture of equal volumes of *alcohol and ether*, and deliquesce in the air.

2. *Ammonia, potassium hydroxide, sodium hydroxide, alkali carbonates,* and *sodium phosphate* show nearly the same reactions with calcium as with barium salts. Recently precipitated CALCIUM CARBONATE, $CaCO_3$, is bulky and amorphous, but after a time, or immediately upon the application of heat, it shrinks and assumes a crystalline form. Recently precipitated calcium

carbonate dissolves somewhat readily in solution of ammonium chloride; but the solution speedily becomes turbid, and deposits the greater part of the dissolved salt in a crystalline form.

3. In highly concentrated solutions, *sulphuric acid* and *sodium sulphate* immediately produce white precipitates of CALCIUM SULPHATE, $CaSO_4.2H_2O$, which redissolve completely in a large proportion of water, and are far more soluble in acids. In less concentrated solutions, the precipitates are formed only after the lapse of some time, and no precipitation whatever takes place in dilute solutions. Solutions of calcium sulphate, of course, cannot produce a precipitate in calcium salts; but even a cold saturated solution of potassium sulphate, mixed with 3 parts of water, produces a precipitate only after standing from twelve to twenty-four hours. In solutions of calcium salts which are so very dilute that sulphuric acid has no apparent action on them, a precipitate will form upon addition of 2 volumes of alcohol, either immediately or after the lapse of some time. Calcium sulphate dissolves in a large amount of a concentrated solution of ammonium sulphate, but this takes place completely only when it is not mixed with barium or strontium sulphate.

4. *Hydrofluosilicic acid* does not precipitate calcium salts, even when an equal volume of alcohol is added.

5. *Ammonium oxalate* produces a white, pulverulent precipitate of CALCIUM OXALATE. If the fluids are in any degree concentrated or hot, the precipitate, $CaC_2O_4.H_2O$, forms at once; but if they are very dilute and cold, it forms only after some time, in the latter case being more distinctly crystalline and consisting of a mixture of the above salt with $CaC_2O_4.3H_2O$. Calcium oxalate dissolves readily in hydrochloric and nitric acids, but acetic and oxalic acids fail to dissolve it to any considerable extent.

6. *Potassium chromate* produces no precipitate at first, even in very concentrated solutions of calcium salts. Only after long standing does CALCIUM CHROMATE, $CaCrO_4.2H_2O$, separate as a yellow, crystalline precipitate. Solutions which are at all dilute do not give a precipitate, but if 2 or 3 volumes of alcohol are added, an immediate precipitation follows in solutions which are not extremely dilute. Calcium solutions

containing free acetic acid are not precipitated, even upon the addition of alcohol. Potassium dichromate does not precipitate even very concentrated solutions.

7. Soluble calcium salts when heated with aqueous *alcohol* impart to its flame a YELLOWISH-RED color, which may be mistaken for that produced by strontium.

8. If calcium salts are held in the fusing zone of the BUNSEN *gas flame*, or in the inner *alcohol blowpipe flame*, they impart to the flame a YELLOWISH-RED color. This reaction is most distinct with calcium chloride, while calcium sulphate shows it only after its incipient decomposition, and calcium carbonate most distinctly after the escape of the carbonic acid. Compounds of calcium with fixed acids do not color flame, but those which are decomposed by hydrochloric acid will show the reaction after being moistened with that acid. In such cases, the reaction is promoted by flattening the loop of the platinum wire, placing a small portion of the calcium compound upon it, letting it frit, adding a drop of hydrochloric acid, which remains hanging to the loop, and then thrusting the latter in the fusing zone. The reaction appears most distinctly at the instant when the drop disappears, having evaporated without boiling as in LEIDENFROST'S phenomenon (BUNSEN). Viewed through *green glass*, the calcium coloration of the flame appears siskin-green on bringing the sample moistened with hydrochloric acid into the flame (difference between calcium and strontium, the latter substance under similar circumstances showing a very faint yellow (MERZ). In presence of barium, the calcium reaction shows only upon the first introduction of the sample into the flame. The *calcium spectrum* is shown in Plate I. The intensely green line β is particularly characteristic, also the intense orange line α. It requires a very good apparatus to show the indigo-blue line to the right of G in the solar spectrum, as this is much less luminous than the others.

9. With *carbonates* and *acid carbonates of the alkalies*, also with a solution of *potassium carbonate and sulphate*, calcium sulphate shows the same behavior as strontium sulphate.

§ 103.

MAGNESIUM, Mg. (*Oxide, Magnesia*, MgO.)

1. MAGNESIUM is silver-white, hard, malleable, of 1.743 sp. gr. It melts at a moderate red heat, and volatilizes at a white heat. When ignited in the air, it burns with a dazzling white flame to magnesium oxide. It preserves its luster in dry air, but gradually becomes coated with hydroxide when exposed to moist air. Pure water is not decomposed by magnesium at the ordinary temperature, but in water acidulated with hydrochloric or sulphuric acid, magnesium dissolves rapidly with evolution of hydrogen.

2. MAGNESIUM OXIDE and HYDROXIDE are white powders of far greater bulk than the other oxides and hydroxides of this group, and are nearly insoluble in both cold and hot water. The hydroxide loses its water upon ignition.

3. Some of the SALTS OF MAGNESIUM are soluble in water, while others are insoluble in that fluid. The soluble salts have a nauseous, bitter taste, and the normal salts do not alter vegetable colors. With the exception of the sulphate, they undergo decomposition when gently ignited, and the greater part of them, even upon simple evaporation of their solutions. Magnesium sulphate loses its acid at a white heat. Nearly all the magnesium salts which are insoluble in water dissolve readily in hydrochloric acid.

4. *Ammonia* throws down from the solutions of normal salts part of the magnesium as HYDROXIDE, $Mg(OH)_2$, in the form of a white, bulky precipitate. The rest of the magnesium remains in solution as a double salt, *i.e.*, in combination with the ammonium salt which is formed by the reaction. It is owing to this tendency of magnesium salts to form such double salts with ammonium compounds that ammonia fails to precipitate them in presence of a sufficient proportion of an ammonium salt with neutral reaction; or, what amounts to the same thing, that ammonia produces no precipitate in solutions of magnesium containing a sufficient quantity of free acid, and that precipitates produced by ammonia in neutral solutions of magnesium are redissolved upon the addition of ammonium chloride. It should be borne in mind

that in solutions containing only 1 equivalent of an ammonium salt (ammonium chloride or sulphate) to 1 equivalent of magnesium salt, although no precipitate is produced by the addition of a slight excess of ammonia, a portion of the magnesium is, however, thrown down on the addition of a large excess of ammonia.

5. *Potassium*, *sodium*, *barium*, and *calcium hydroxides* throw down MAGNESIUM HYDROXIDE. The separation of this precipitate is greatly promoted by boiling the mixture. Ammonium chloride and similar ammonium salts redissolve the washed hydroxide. If the ammonium salts are added in sufficient quantity to the magnesium solution before the addition of the precipitant, small quantities of the latter fail altogether to produce a precipitate. However, upon boiling the solution afterwards with an excess of potassium or sodium hydroxide, the precipitate will, of course, make its appearance, since this process causes the decomposition of the ammonium salt, thus removing the agent which retains the magnesium hydroxide in solution. It should be remembered that magnesium hydroxide is more soluble in solutions of potassium chloride, sodium chloride, potassium sulphate, and sodium sulphate, than in water, and on this account, its precipitation is less complete when these salts are present in large quantities. From such solutions, however, the magnesium is thrown down, for the most part, by an excess of solution of potassium or sodium hydroxide.

6. *Potassium carbonate* and *sodium carbonate* produce in neutral solutions a white precipitate of BASIC MAGNESIUM CARBONATE, $4MgCO_3.Mg(OH)_2.xH_2O$. One fifth of the carbonic acid of the decomposed alkali carbonate is liberated in the process, and combines with a portion of the magnesium carbonate to form bicarbonate, which remains in solution. This acid carbonate is decomposed by boiling, and an additional precipitate formed, consisting of $MgCO_3.3H_2O$, while carbon dioxide escapes. Application of heat, therefore, promotes the separation, and increases the quantity of the precipitate. Ammonium chloride and other similar ammonium salts, when present in sufficient quantity, prevent this precipitation also, and readily redissolve the precipitates after they have been washed.

7. If magnesium solutions are mixed with *ammonium carbonate*, the liquid always remains clear at first; but after standing, it deposits a crystalline precipitate, more or less quickly according to the concentration of the solution. When the ammonium carbonate is in slight excess, the precipitate consists of magnesium carbonate, $MgCO_3.3H_2O$; but when the ammonium carbonate is in large excess, it consists of AMMONIUM MAGNESIUM CARBONATE, $(NH_4)_2Mg(CO_3)_2.4H_2O$. In highly dilute solutions, this precipitate will not form. Addition of ammonia and of excess of ammonium carbonate promotes its separation. Ammonium chloride prevents the formation of the precipitate, except in concentrated solutions.

8. *Sodium phosphate* precipitates from magnesium solutions, if not too dilute, HYDROGEN MAGNESIUM PHOSPHATE, $HMgPO_4.7H_2O$, as a white powder. Upon boiling, magnesium phosphate, $Mg_3(PO_4)_2.7H_2O$, separates even from rather dilute solutions. But if the addition of the precipitant is preceded by that of *ammonium chloride* and *ammonia*, a white, crystalline precipitate of AMMONIUM MAGNESIUM PHOSPHATE, $NH_4MgPO_4.6H_2O$, will separate even from very dilute solutions. Its formation in dilute solutions may be greatly promoted and accelerated by stirring with a glass rod, and should the solution be so extremely dilute as to forbid the formation of a precipitate, yet the lines of direction in which the glass rod has moved along the inside of the vessel will, after the lapse of some time, appear distinctly as white streaks (soluble in hydrochloric acid). Water and solutions of ammonium salts dissolve the precipitate but very slightly, yet it is readily soluble in acids, even in acetic acid. In water containing ammonia, it may be considered practically insoluble. Instead of hydrogen sodium phosphate, *hydrogen sodium ammonium phosphate* is a very good reagent to use.

9. *Ammonium oxalate* produces no precipitate in highly dilute solutions of magnesium salts. In less dilute solutions, no precipitate is formed at first, but after standing some time, crystalline crusts of various *double oxalates of ammonium and magnesium* make their appearance. In highly concentrated solutions, ammonium oxalate very speedily produces precipitates of magnesium oxalate, $MgC_2O_4.2H_2O$, which contain small quantities of the double salts previously mentioned.

Ammonium chloride, especially in presence of free ammonia, interferes with the formation of these precipitates, but in general will not absolutely prevent it.

10. *Sulphuric acid, hydrofluosilicic acid,* and *potassium chromate* do not precipitate salts of magnesium.

11. Salts of magnesium do not color flames.

§ 104.

Recapitulation and Remarks.—The difficult solubility of magnesium hydroxide, the ready solubility of the sulphate (unless present in the natural form, *i.e.*, as kieserite, which contains one molecule of water), and the disposition of magnesium salts to form double salts with ammonium compounds, are the three principal points in which magnesium differs from the other alkali-earth metals. To detect magnesium in solutions containing all the alkali-earth metals, we always first remove the barium, strontium, and calcium. This is effected most conveniently by means of ammonium carbonate, with addition of some ammonia and ammonium chloride, and application of heat; since by this process, the barium, strontium, and calcium are obtained in a form of combination suited for further examination. If the solutions are somewhat dilute, and the precipitated fluid is filtered after about an hour, the carbonates of barium, strontium, and calcium are obtained on the filter, while all the magnesium is found in the filtrate. But as ammonium chloride dissolves a little barium carbonate, and also a little calcium carbonate, though much less of the latter than of the former, trifling quantities of these metals are found in the filtrate. Moreover, where only traces of them are present, they may remain wholly in solution. In accurate experiments, therefore, the complete separation is effected in the following way: Divide the filtrate into three portions, test one portion with a few drops of dilute sulphuric acid for the trace of barium which it may contain, and another portion with ammonium oxalate for the minute trace of calcium which may have remained in solution. If the two reagents produce no turbidity, even after some time, test the third portion with sodium phosphate and ammonia for MAGNESIUM. If, however, one of the reagents causes turbidity,

filter off the gradually subsiding precipitate, and test the filtrate for magnesium. Should both reagents produce precipitates, mix the first two portions together, which in any case must still be alkaline, filter after some time, and then test the filtrate for magnesium. To make sure that the precipitate thrown down by ammonium oxalate is actually calcium oxalate, and not, as it might be, oxalate of ammonium and magnesium, dissolve it in a very little hydrochloric acid, and add dilute sulphuric acid, and then alcohol.

To show the presence of barium, strontium, and calcium in the precipitate produced by ammonium carbonate, dissolve the precipitate in an exactly sufficient amount of dilute nitric acid, evaporate the solution in a small porcelain dish to dryness, heat this upon an iron plate for 10 or 15 minutes rather strongly (the temperature may rise to 180° without injury) until the residue no longer has an odor of nitric acid, and a cold glass plate, placed upon the dish for a few seconds, no longer shows a coating of moisture. Triturate the contents of the dish immediately after cooling, at first dry, then after the addition of about 5 to 10 cc of a mixture of equal volumes of absolute alcohol and ether. Filter the solution after a few minutes, and wash the residue four times with small quantities of the ether-alcohol mixture. The residue now contains the barium and strontium nitrates, to which a small amount of calcium nitrate may still adhere; while the filtrate contains the calcium nitrate, with which there may be a slight trace of strontium nitrate if the operation has not been performed with sufficient care.

Add 2 drops of dilute sulphuric acid to the ether-alcohol solution. If a considerable amount of precipitate results, this must be *calcium* sulphate, and it is unnecessary to test further for calcium. If, however, the precipitate should be very small, it might originate from the traces of strontium which had possibly gone into the ether-alcohol solution. In this case, therefore, add about 4 cc of water to the solution, evaporate off the ether and alcohol, add a few drops of ammonia and about 1 g of solid ammonium sulphate, heat to boiling, filter through a small filter, add to the filtrate a drop of acetic acid, so that it just reddens litmus-paper, then a few drops of ammonium oxalate. If CALCIUM is present,

a precipitate of calcium oxalate is formed immediately, or, if only very small amounts are present, after standing for some time. Any error on account of the very small amount of strontium possibly present is excluded, because the traces of strontium sulphate which dissolve in a concentrated solution of ammonium sulphate are not precipitated by ammonium oxalate in the presence of a little free acetic acid.

Dissolve the barium and strontium nitrates with the aid of heat in 70 to 100 parts of water, filter if necessary, acidify with 3 or 4 drops of acetic acid, heat to boiling, add gradually potassium chromate until the solution shows a yellow color, and boil up once more. If an odor of acetic acid then appears, add some more potassium chromate. If BARIUM is present, a bright yellow precipitate appears at once, or if only very small amounts are present, after standing a short time. Let it stand for about an hour, filter, and add some ammonia to a portion of the filtrate, then add ammonium carbonate. If a considerable amount of precipitate results, this can only be strontium carbonate, and it is unnecessary, therefore, to make further tests for strontium. If, on the other hand, no precipitate or only a very small one is produced, add 1 or 2 drops of nitric acid to the main part of the filtrate, concentrate to 10 or 20 cc, and then add ammonia and ammonium carbonate. If no precipitate is now found, strontium is not present; but if there is a small precipitate, this may be strontium, but it may possibly be due to traces of calcium which are still present here. Filter off the small precipitate, wash it, dissolve it in a few drops of dilute hydrochloric acid, and evaporate the solution to dryness. Dissolve the small residue of neutral chloride or chlorides in 1 or 2 cc of a mixture of 3 parts of water and 1 part of alcohol (which should be kept on hand), add a drop of potassium chromate solution, and heat until boiling just begins. If STRONTIUM is present, a finely divided, yellow precipitate of strontium chromate separates immediately or after standing a short time in a warm place (W. FRESENIUS and F. RUPPERT).

The separation is accomplished just as well but less simply as follows: Dissolve the precipitate consisting of barium, strontium, and calcium carbonates in acetic acid, remove most of the excess of this by evaporation, and after addition

of water precipitate the barium from the solution, which must always contain some free acetic acid, by adding an excess of potassium chromate. In order to effect a good separation of strontium from calcium, it is then necessary to precipitate both these metals with ammonium carbonate, to convert the carbonates into dry nitrates, and to separate these with ether-alcohol, thus making the whole process less simple than the previous one.

For the detection of small amounts of calcium in the presence of large amounts of barium and strontium, the following method can also be used: Precipitate the solution, to which some hydrochloric acid is added, while hot with dilute sulphuric acid, filter off the precipitate, first make the filtrate alkaline with ammonia, then acidify it with acetic acid and add ammonium oxalate. A resulting precipitate, often formed only after long standing, shows the presence of calcium, because the traces of strontium sulphate which have remained in solution upon its precipitation with sulphuric acid are not precipitated by ammonium oxalate from the solution containing some free acetic acid.

The methods formerly practised for the separation of barium, strontium, and calcium, or for the recognition of one of these metals in the presence of another, being based upon the varying deportment of the solutions of their salts to calcium sulphate solution, upon the separation of the dry chlorides by alcohol, and upon the separation of strontium and calcium sulphates by ammonium sulphate, are much less exact than those described, as is already evident from what has been stated in relation to the reactions of the separate metals. The separation of barium from strontium, which is based upon the varying deportment of the sulphates to a solution of ammonium carbonate or to a mixture of potassium carbonate and sulphate, is also not to be recommended, since in the predominance of barium sulphate, a portion of the strontium sulphate remains undecomposed, while in the predominance of strontium sulphate, barium sulphate is also converted into carbonate. The separation of barium from calcium succeeds better upon this basis, but even this is not fully exact.

If the sulphates of the alkali-earth metals present them-

selves for investigation, the mass is first extracted with small quantities of boiling water. The solution contains the whole of the magnesium sulphate, if this is not present as kieserite, besides a small quantity of calcium sulphate. The residue is fused with 4 parts of potassium-sodium carbonate in a platinum crucible, the mass is treated with boiling water, and the resulting carbonates are filtered and washed. In order to detect the alkali-earth metals in their phosphates, it is most advantageous to decompose these by means of ferric chloride with the addition of sodium acetate (see Section III, under phosphoric acid). They are detected in their oxalates after changing them by ignition into carbonates. The fluorides and silicofluorides of the alkali-earth metals are first converted into sulphates by heating with concentrated sulphuric acid.

The detection of barium, strontium, and calcium by the wet way, as above described, is somewhat tedious, but it gives an approximate idea of the relative quantities. By means of the spectroscope, these metals are much more readily detected even when all three are present together. According to the nature of the acid, the sample is either introduced into the flame directly, or after previous ignition in the reducing flame and moistening with hydrochloric acid. To detect very minute quantities of barium and strontium in presence of large quantities of calcium, ignite a few grams of the mixed carbonates for several minutes in a platinum crucible strongly over the blast-lamp (whereby barium and strontium carbonates become caustic much more readily than would be the case in the absence of calcium carbonate), extract the ignited mass by boiling with a little distilled water, filter, evaporate with hydrochloric acid to dryness, and examine the residue by spectrum analysis (Engelbach). If traces of calcium and strontium are to be detected in barium minerals, convert the metals into chlorides, extract these with very small amounts of absolute alcohol, and examine by spectrum analysis the residue left upon evaporation. In dealing with the detection of traces of calcium and barium in strontium minerals, extract the chlorides, first with cold, then with hot alcohol. In the first extract, the calcium is to be found; in the succeed-

ing ones, strontium, while barium is in the last or in the residue. (The tests should be ignited in the reducing flame, then moistened with hydrochloric acid, and brought into the flame.) (BUNSEN.)

Concerning the detection of magnesium by means of an absorption-spectrum, compare H. W. VOGEL and F. VON LEPEL, Zeitschr. f. analyt. Chem., **17**, 89. Barium, strontium, calcium, and magnesium can also be detected by microchemical methods, even when only small amounts are present. (Compare HAUSHOFER, pp. 15, 32, 92, and 121, and BEHRENS, Zeitschr. f. analyt. Chem., **30**, 139, 145, 146, and 148.)

§ 105.

THIRD GROUP.

More common metals: ALUMINIUM, CHROMIUM.

Rarer metals: BERYLLIUM, THORIUM, ZIRCONIUM, YTTRIUM, CERIUM, LANTHANUM, DIDYMIUM, TITANIUM, TANTALUM, NIOBIUM.

Properties of the Group. — The oxides and hydroxides of the third group are insoluble in water. The sulphides cannot be produced in the wet way. Hydrogen sulphide, therefore, fails to precipitate the solutions of the salts. From solutions of the salts in which the metals of the third group constitute the base,* ammonium sulphide throws down the hydroxides in the same way as ammonia. The reaction with ammonium sulphide distinguishes the metals of the third group from those of the two preceding ones.

* The oxides of almost all the metals of the third group are able to combine with acids as well as with bases to form salts; for example, alumina with potassium oxide forms potassium aluminate, while with sulphuric acid, aluminium sulphate is formed. Some of these elements, therefore, stand upon the boundary between acid-forming and basic elements. The oxides of titanium, tantalum, and niobium are called acids, because they stand near the acids in their properties.

Special Reactions of the More Common Metals of the Third Group.

§ 106.

a. ALUMINIUM, Al. (*Oxide, Alumina*, Al_2O_3.)

1. ALUMINIUM is nearly white. It is not oxidized by the action of the air, in compact masses scarcely even upon ignition. It may be filed, is very malleable, and its specific gravity is only 2.67. It is fusible at a bright red heat. It does not decompose boiling water. Aluminium dissolves readily in hydrochloric acid, as well as in hot solution of potassium hydroxide, with evolution of hydrogen. Nitric acid dissolves it but slowly, even with the aid of heat.

2. ALUMINIUM OXIDE is non-volatile and colorless, and the HYDROXIDE is also colorless. Alumina dissolves in dilute acids slowly and with very great difficulty, but more readily in concentrated, hot hydrochloric acid. In fusing potassium disulphate, it dissolves readily to a mass soluble in water. In the amorphous condition, the hydroxide is readily soluble in acids, but in the crystalline state, it dissolves in them with very great difficulty. By ignition with alkalies, an aluminate is formed which readily dissolves in acids. By igniting alumina mixed with carbon in a current of chlorine, or by the action of carbon tetrachloride, CCl_4, upon alumina below a red heat (DEMARÇAY), aluminium chloride, $AlCl_3$, is obtained as a sublimate.

3. The ALUMINIUM OXYGEN SALTS are colorless and non-volatile; some of them are soluble, others insoluble. The anhydrous chloride is solid, colorless, crystalline, volatile, and easily soluble in water. The soluble oxygen salts have a sweetish, astringent taste, redden litmus-paper, and lose their acid upon ignition. With the exception of certain native compounds, the salts insoluble in water are dissolved by hydrochloric acid, while the aluminium compounds which are insoluble in hydrochloric acid are made soluble by ignition with sodium-potassium carbonate or potassium disulphate. Their decomposition and solution may be also effected by heating them, reduced to a fine powder, with hydrochloric

acid of 25 per cent, or with a mixture of 3 parts by weight of sulphuric acid and 1 part by weight of water, in sealed glass tubes, from 200° to 210° for two hours (A. MITSCHERLICH).

4. From solutions of aluminium salts, *potassium* and *sodium hydroxides* throw down a bulky precipitate of ALUMINIUM HYDROXIDE, $Al(OH)_3$, which contains alkali and generally also an admixture of basic salt, and redissolves readily and completely in an excess of the precipitant. The solution of alkaline aluminate thus formed remains clear upon boiling, but the aluminium hydroxide is precipitated again by the addition of sufficient ammonium chloride (compare § 56). This precipitation takes place even in the cold, but is more complete upon heating. The precipitate does not dissolve in excess of ammonium chloride, and ammonium salts do not interfere with the precipitation by potassium or sodium hydroxide.

5. *Ammonia* and *ammonium sulphide* also produce a precipitate of ALUMINIUM HYDROXIDE, which contains ammonia and an admixture of basic salt. The precipitate redissolves to some extent in a large excess of the precipitant, but this solubility is lessened by ammonium salts. Boiling promotes the precipitation, as it drives off the excess of ammonia. This deportment accounts for the complete precipitation of aluminium hydroxide from solution in potassium or sodium hydroxide by an excess of ammonium chloride, especially when the solution is boiled.

6. *Alkali carbonates* precipitate BASIC ALUMINIUM CARBONATE, which is slightly soluble in excess of fixed alkali carbonate, and still less soluble in excess of ammonium carbonate. Boiling promotes precipitation by the latter.

7. If the solution of an aluminium salt is digested with finely divided *barium carbonate*, the greater part of the acid of the aluminium salt combines with the barium, the liberated carbonic acid escapes, and the aluminium precipitates completely as HYDROXIDE MIXED WITH BASIC SALT. Even digestion in the cold suffices to produce this reaction.

N.B. to 4, 5, 6, and 7.—Tartaric, citric, and other non-volatile organic acids completely prevent the precipitation of aluminium as hydroxide or basic salt, when they are present in considerable quantity. The presence of sugar and similar

organic substances interferes with the completeness of the precipitation.

8. *Sodium phosphate* precipitates ALUMINIUM PHOSPHATE, $AlPO_4.4H_2O$, from solutions of aluminium salts. The bulky, white precipitate is readily soluble in potassium or sodium hydroxide solution, but difficultly so in ammonia, and scarcely at all when ammonium salts are present. Ammonium chloride, therefore, precipitates it from its solution in potassium or sodium hydroxide. The precipitate is readily soluble in hydrochloric or nitric acid, but not in acetic acid (difference from aluminium hydroxide). Therefore, sodium acetate precipitates it from its solution in hydrochloric acid if the latter is not too predominant. Tartaric acid, sugar, etc., do not prevent the precipitation of aluminium phosphate, but citric acid does prevent it (GROTHE).

9. *Oxalic acid* and its salts do not precipitate solutions of aluminium.

10. *Potassium sulphate*, added to very concentrated solutions of salts of aluminium, occasions the gradual separation of aluminium potassium sulphate, $K_2SO_4.Al_2(SO_4)_3.24H_2O$, in the form of crystals or a crystalline powder.

11. If aluminium oxide or a compound of it is ignited upon charcoal before the blowpipe, and afterwards moistened with a solution of *cobalt nitrate*, and then again strongly ignited, an unfused mass of a deep SKY-BLUE color is produced, which consists of a compound of the two oxides. The blue color becomes distinct only upon cooling. By candlelight it appears violet. This reaction is to be relied on, in a measure, only in the case of infusible or difficultly fusible compounds of aluminium nearly free from other metals. It is never quite decisive, since cobalt solution may give a blue color under similar circumstances, not only with readily fusible compounds, but also with certain infusible compounds free from aluminium, such as the normal phosphates of the alkali-earth metals.

§ 107.

b. CHROMIUM, Cr. (*Chromic oxide*, Cr_2O_3.)

1. CHROMIC OXIDE is a green, CHROMIC HYDROXIDE, usually a bluish gray-green powder. The hydroxide dissolves readily in acids, while the non-ignited chromic oxide dissolves more difficultly, and ignited chromic oxide is almost insoluble. When chromic oxide mixed with carbon is ignited in a stream of chlorine, or when it is heated below redness in the vapor of carbon tetrachloride (DE-MARÇAY), it yields crystalline, reddish-violet chromium chloride, $CrCl_3$.

2. The CHROMIC SALTS have a green or violet color. Many of them are soluble in water, and most of them dissolve in hydrochloric acid. The solutions exhibit a fine green or a dark violet color, the latter, however, changing to green upon heating. The chromic oxygen salts with volatile acids are decomposed upon ignition, the acids being expelled. The chromic salts which are soluble in water redden litmus. Anhydrous chromic chloride is crystalline, violet-colored, insoluble in water and in acids, and volatilizes with difficulty.

3. In the green as well as in the violet solutions, *potassium and sodium hydroxides* produce a bluish-green precipitate of CHROMIC HYDROXIDE, which dissolves readily and completely in an excess of the precipitant, imparting to the fluid an emerald-green tint. Upon *long-continued* ebullition of this solution, the whole of the hydroxide separates again, and the supernatant fluid appears perfectly colorless. The same reprecipitation takes place if ammonium chloride is added to the alkaline solution. Application of heat promotes the separation of the precipitate.

4. *Ammonia* and also *ammonium sulphide* produce in green solutions a grayish-green, in violet solutions a grayish-blue, precipitate of CHROMIC HYDROXIDE. The former precipitate dissolves in cold hydrochloric acid to a reddish-violet fluid, the latter to a bluish-violet fluid. Other circumstances (concentration, way of adding the ammonia, etc.) also exercise some influence upon the composition and color of these hydroxides. In the cold, a small portion of the hydroxide

redissolves in an excess of the precipitant, imparting to the liquid a peach-blossom red tint; but if, after the addition of ammonia in excess, heat is applied to the mixture, the precipitation is complete.

5. *Alkali carbonates* precipitate BASIC CHROMIC CARBONATE, which redissolves with difficulty and slowly in an excess of the precipitant.

6. *Barium carbonate* precipitates the whole of the chromium as a GREENISH HYDROXIDE MIXED WITH BASIC SALT. The precipitation takes place in the cold, but is complete only after long-continued digestion.

7. *Sodium phosphate* when added to neutral or weakly acid, either green or violet solutions of chromic salts (but not chromic oxalate solutions), to which sodium acetate has been added in excess, upon boiling precipitates all the chromium as *chromium phosphate*, $CrPO_4.3H_2O$, in the form of a light green precipitate (A. CARNOT).

N. B. to 4, 5, 6, and 7.—The precipitation of chromium hydroxide by ammonia, both in green and violet solutions, is interfered with more or less by tartaric acid, citric acid, and sugar, as well as by oxalic acid. After long standing, the precipitates resulting at first occasionally redissolve completely, forming violet or green solutions. The precipitation by sodium carbonate, as well as by sodium phosphate, is often wholly prevented by the acids which have been mentioned, and in their presence, the precipitation by barium carbonate is incomplete. A solution of a chromic salt which has been boiled for a considerable time with the addition of sodium acetate is not precipitated in the cold either by alkali-metal hydroxides, carbonates, or phosphates, barium carbonate or ammonium sulphide, but precipitation does take place by boiling (REINITZER).

8. If a solution of chromic hydroxide in caustic potash or soda is mixed with some *lead dioxide* in excess, and the mixture is boiled a short time, the chromic hydroxide is oxidized to chromic acid. A yellow fluid is therefore obtained on filtering, which consists of a solution of LEAD CHROMATE in caustic potash or soda. Upon acidifying this liquid with acetic acid, the lead chromate separates as a yellow precipitate (CHANCEL).

9. If a solution containing a chromic salt is allowed to flow

into a hot sodium carbonate solution to which *potassium permanganate* has been added, and the whole is boiled for a short time, chromic oxide is changed to chromic acid. If a few drops of alcohol are now added in order to reduce the excess of the permanganate, and the resulting hydrated manganese dioxide is filtered off, any considerable amount of chromium can be recognized by the yellow coloration of the filtrate, due to SODIUM CHROMATE (DONATH).

10. The fusion of chromic oxide or of any chromic compound with *sodium nitrate and carbonate*, or still better, with *potassium chlorate and sodium carbonate* or with *sodium peroxide* (HEMPEL), gives rise to the formation of yellow ALKALI CHROMATE, which dissolves in water to an intensely yellow fluid.

N. B. to 8, 9, and 10.—If the amount of chromium is so minute that the filtrates do not show a yellow color, any trace of chromic acid they contain may often be detected by concentrating the liquid, and applying the methods recommended under chromic acid for the detection of the smallest amounts of that substance.

11. In both the oxidizing and reducing flames of the blowpipe, *sodium metaphosphate* dissolves chromic oxide and chromic salts to clear beads of a faint yellowish-green tint, which upon cooling change to EMERALD GREEN. Chromic compounds show a similar reaction with *borax*. The BUNSEN gas flame (§ 16) or the blowpipe flame is used for the experiment.

§ 108.

Recapitulation and Remarks.—The solubility of aluminium hydroxide in sodium and potassium hydroxide solutions (or also in barium hydroxide solution, which should be used when no alkali-metal hydroxides free from silicic acid and alumina are available, BECKMANN), and its reprecipitation from the alkaline solutions by ammonium chloride, afford a safe means of detecting aluminium in the absence of chromium. But if the latter is present, which is seen either by the color of the solution or by the reaction with sodium metaphosphate, it must be removed before aluminium can be tested for. This separation of chromium from aluminium is effected most completely by fusing 1 part of the mixed oxides with 2 parts of sodium carbonate and 2 parts of potassium chlorate (which

may be done in a platinum crucible), and the yellow mass obtained is boiled with water. By this process, the whole of the chromium is dissolved as potassium chromate, and part of the aluminium as potassium aluminate, the rest of the aluminium remaining undissolved. If the solution is acidified with nitric acid, it acquires a reddish-yellow tint; and if ammonia is then added to feebly alkaline reaction, the dissolved portion of the aluminium separates.

If it is preferred to change the chromium oxide to chromic acid in the wet way in order to make the separation from aluminium, the solution of both in potassium or sodium hydroxide may be boiled with potassium permanganate, then after reduction, (by means of some alcohol), of the permanganate added in excess, filtering off the hydrated manganese dioxide and acidifying the filtrate with nitric acid, aluminium hydroxide can be precipitated by ammonia. The chromic oxide can also be readily converted into alkali-metal chromate by gently warming the alkaline solution of both oxides with hydrogen peroxide.

The precipitation of chromic hydroxide, effected by boiling its solution in potassium or sodium hydroxide, is also sufficiently exact if the ebullition is continued long enough. Still it is often liable to mislead in cases where only little chromic salt is present, or where the solution contains organic matter, even though in small proportion only. Attention should here be called to the fact that the solubility of chromic hydroxide in an excess of cold solution of potassium or sodium hydroxide is considerably impaired by the presence of other hydroxides (manganous, nickelous, cobaltous, zinc, ferric, lead, calcium, magnesium hydroxides, etc.). If these happen to be present in large excess, they may altogether prevent the solution of the chromic hydroxide in caustic potash or soda. Lastly, the influence of non-volatile organic acids, sugar, etc., upon the precipitation of aluminium and chromium hydroxides by ammonia, etc., must be remembered. If organic substances are present, therefore, ignite, fuse the residue with sodium carbonate and potassium chlorate, and proceed as directed before.

Concerning the detection of very small traces of aluminium by means of cochineal tincture, compare LUCKOW, Zeitschr. f.

analyt. Chem., **3**, 362; by means of an alcoholic solution of morin and the fluorescence produced in it, compare GOPPELSRÖDER, *ibid.*, **7**, 208; by means of tincture of logwood, see HORSLEY and SCHUMACHER-KOPP, *ibid.*, **31**, 222; in respect to the detection of aluminium by an absorption-spectrum, see H. W. VOGEL, *ibid.*, **15**, 332, and **17**, 89. Concerning the microchemical detection of aluminium and chromium, see HAUSHOFER, pp. 12 and 47, and BEHRENS, Zeitschr. f. analyt. Chem., **30**, 159 and 161.

Special Reactions of the Rarer Metals of the Third Group.

§ 109.

1. BERYLLIUM, Be, or GLUCINUM, Gl. (*Oxide*, BeO.)

Beryllium is a rare metal found in the form of a silicate in phenacite, and with other silicates in beryl, euclase, and some other rare minerals. Beryllium oxide is a white, tasteless powder, insoluble in water. The ignited earth dissolves slowly but completely in acids, and is readily soluble after fusion with potassium disulphate. The hydroxide dissolves readily in acids. The compounds of beryllium very much resemble those of aluminium. The soluble beryllium salts have a sweet, astringent taste, their reaction is acid, and the solutions are colorless. The native silicates of beryllium are completely decomposed by fusing with 4 parts of sodium-potassium carbonate, and most of them also by heating with concentrated sulphuric acid. Anhydrous beryllium chloride, obtained by igniting beryllium oxide mixed with carbon in a stream of chlorine, also by moderate ignition in carbon tetrachloride (L. MEYER and R. WILKENS), is white, crystalline, capable of being sublimed, and easily soluble in water. From solution of beryllium salts, *potassium* and *sodium hydroxides*, *ammonia*, and *ammonium sulphide* throw down the white, flocculent hydroxide, which is but slightly soluble in ammonia, yet dissolves readily in solution of caustic potash or soda, from which solution it is precipitated again by ammonium chloride. The concentrated, alkaline solutions remain clear on boiling, but from more dilute, alkaline solutions, the whole of the beryllium separates upon continued ebullition (difference between beryllium and aluminium,* but this is only a means for complete separation when pure potas-

* [This test may fail when precipitated beryllium phosphate, which dissolves readily in caustic alkalies, is so treated. To apply the test, fuse the beryllium phosphate with sodium carbonate, treat the mass with hot water, and filter. The whole of the beryllium oxide, free from phosphoric acid, is thus obtained. Dissolve this in hydrochloric acid, evaporate to very small bulk to remove practically all the free acid, add pure potassium hydroxide slowly to the cold, concentrated solution until the beryllium hydroxide has redissolved, filter if necessary, dilute very largely, and boil.]

sium, not sodium hydroxide, is used, and the dilution is not too great*). *Tartaric acid* prevents the precipitation by alkalies. By continued boiling with *ammonium chloride*, the freshly precipitated hydroxide dissolves as beryllium chloride, driving off ammonia (difference from aluminium). *Alkali carbonates* precipitate white beryllium carbonate, which redissolves in a great excess of sodium or potassium carbonate, and in a much less considerable excess of ammonium carbonate (especially characteristic difference between beryllium and aluminium, but they cannot be completely separated in this way, as in the presence of beryllium, a certain quantity of aluminium dissolves in ammonium carbonate, JOY). Upon boiling these solutions, basic beryllium carbonate separates readily and completely from the solution in ammonium carbonate, but only upon dilution and imperfectly (as hydroxide) from the solutions in sodium and potassium carbonate. If the solution of a beryllium salt is treated with *ammonium phosphate* in considerable excess (sodium phosphate does not answer), the resulting precipitate is dissolved in hydrochloric acid, then, while the liquid is constantly heated, ammonia is added drop by drop to neutral reaction (an excess being avoided) and the liquid is then heated to boiling for some time, the precipitate, ammonium beryllium phosphate, which is slimy at first, assumes a crystalline condition, and subsides rapidly. Citric acid does not prevent this reaction (difference from aluminium, which never yields a crystalline precipitate under these conditions, and which is not precipitated at all in the presence of citric acid). The presence of much aluminium prevents the separation of the beryllium precipitate in the presence of citric acid (C. RÖSSLER). *Barium carbonate* precipitates beryllium completely upon boiling, but not upon cold digestion. *Oxalic acid* and *oxalates* do not precipitate beryllium (difference from thorium, zirconium, yttrium, cerium, lanthanum, didymium). When fused with 2 parts of *hydrogen potassium fluoride*, beryllium oxide yields a mass which dissolves in water acidified with hydrofluoric acid. (This reaction serves as a means of separating beryllium from aluminium, for when the latter is similarly treated, it remains insoluble as potassium aluminium fluoride.) For the detection of small amounts of beryllium when present with much aluminium, dissolve the hydroxides in hydrochloric acid, evaporate to dryness, take up the residue with a little water, using a very little hydrochloric acid if necessary, transfer to a tube of strong Bohemian glass which is closed at one end, add potassium sulphate (about 12 parts for 1 part of alumina) and also enough water so that the salt can dissolve upon heating, seal the tube by fusion, warm until everything has dissolved, and heat for half an hour to 180°. After cooling, open the tube, filter off the basic potassium aluminium sulphate, precipitate the solution with ammonia, dissolve the filtered precipitate in hydrochloric acid, add enough citric acid so that ammonia produces no precipitate, and then separate beryllium as crystalline ammonium beryllium phosphate

* A. ZIMMERMANN succeeded in making a complete separation where 0.3 g of the oxides were dissolved in 300 cc of dilute potassium hydroxide. With greater dilution, aluminium hydroxide precipitates with the beryllium.

(C. RÖSSLER). Moistened with solution of *cobalt nitrate*, the beryllium compounds give gray masses upon ignition. Concerning the microchemical detection of beryllium, see HAUSHOFER, p. 23, and BEHRENS, Zeitschr. f. Analyt. Chem., 30, 139; in regard to the spectroscopic detection, see HARTLEY, Jahresbericht d. Chem., 1887, 1, 346.

§ 110.

2. THORIUM, Th. (*Thoria*, ThO_2.)

Thorium is a very rare metal, found in thorite, monazite, etc. The oxide is white or gray. Ignited thoria is soluble upon heating with a mixture of 1 part of concentrated sulphuric acid and 1 part of water; but it is not soluble in other acids, even after fusion with alkalies. When thoria, produced by gently igniting the oxalate, is evaporated with hydrochloric or nitric acid, the corresponding salts are left in a varnish-like form, and at once dissolve completely in water, giving colorless solutions. Hydrochloric and nitric acids precipitate the chloride or nitrate from such solutions, and even sulphuric acid may produce a precipitate in them (BAHR). The moist hydroxide dissolves readily in acids, the dried hydroxide only with difficulty. Thorium chloride is volatile at a nearly white heat. Thorite (thorium silicate) is decomposed by moderately concentrated sulphuric acid, and also by concentrated hydrochloric acid. From solutions of thorium salts, *potassium hydroxide*, *ammonia*, and *ammonium sulphide* precipitate the white hydroxide, which is insoluble in an excess of the precipitant, even of potassium hydroxide (difference from aluminium and beryllium). Tartaric acid prevents the precipitation. *Potassium carbonate* and *ammonium carbonate* precipitate basic thorium carbonate, which readily dissolves in an excess of the precipitant in concentrated solutions, but with difficulty in dilute solutions (difference from aluminium). From the solution in ammonium carbonate, the basic salt separates again even at 50°. *Barium carbonate* precipitates thorium completely. *Hydrofluoric acid* precipitates the fluoride, which at first appears gelatinous, but after a little while, pulverulent. The precipitate is insoluble in water and hydrofluoric acid (difference from aluminium, beryllium, zirconium, and titanium). *Oxalic acid* causes a white precipitate (difference from aluminium and beryllium). The precipitate is not soluble in oxalic acid, and is very slightly soluble in dilute mineral acids (BERZELIUS), but it does dissolve in a solution of ammonium acetate containing free acetic acid (difference from yttrium and cerium). It also dissolves in a boiling, concentrated solution of ammonium oxalate, and is not reprecipitated when the solution is diluted and allowed to cool (difference from cerium, lanthanum, didymium, and yttrium, BUNSEN). A concentrated solution of *potassium sulphate* precipitates thorium slowly but completely (difference from aluminium and beryllium). The precipitate consists of potassium thorium sulphate, which is insoluble in concentrated solution of potassium sulphate, dissolving with difficulty in cold and easily in hot water. Anhydrous,

normal thorium sulphate dissolves in ice-water, but upon warming even to the temperature of the room, it separates in a hydrated, very difficultly soluble condition (difference from aluminium, beryllium, cerium, yttrium). If the hydrated salt is converted by heating into the water-free condition, it dissolves again in ice-water (difference from titanic acid, KRÜSS and NILSON). If thorium hydroxide is suspended in *potassium hydroxide* solution and *chlorine* is led in, it does not dissolve (difference from many other earths, but not from cerium oxide, J. LAWRENCE SMITH). From neutral or slightly acid solutions, on boiling, *sodium thiosulphate* precipitates thorium thiosulphate mixed with sulphur, but the precipitation is not quite complete (difference from yttrium and didymium). Concerning the microchemical detection of thorium, see HAUSHOFER, p. 127, and BEHRENS, Zeitschr. f. analyt. Chem., **30**, 157.

§ 111.

3. ZIRCONIUM, Zr. (*Zirconia*, ZrO_2.)

Zirconium occurs in zircon, eudialite, and some other rare minerals. Zirconia is a white, infusible powder, which glows upon ignition, and is insoluble in hydrochloric acid, but is soluble upon addition of water after long-continued heating with 2 parts of concentrated sulphuric acid and 1 part of water. Soluble zirconium salts are also obtained by fusion with alkali-metal disulphates or with hydrogen potassium fluoride. The hydroxide resembles aluminium hydroxide, dissolving readily in hydrochloric acid when precipitated cold and still moist, but with difficulty when precipitated hot or after drying. The zirconium salts soluble in water redden litmus, and their solutions are colorless. The native zirconium silicates may be decomposed by fusion with sodium carbonate. The finely elutriated silicate is fused at a high temperature, together with 4 parts of sodium carbonate. The fused mass gives sodium silicate to water, a sandy sodium zirconate being left behind, which is washed and dissolved in hydrochloric acid. Zircon may be easily decomposed by fusion with hydrogen potassium fluoride at a red heat, potassium silicofluoride and potassium zirconium fluoride being produced. When zirconia is mixed with carbon and ignited in a stream of chlorine, or is treated for a long time below redness with carbon tetrachloride (DEMARÇAY), zirconium chloride, $ZrCl_4$, is produced, which is solid, white, capable of being sublimed, and soluble in water. *Potassium* and *sodium hydroxides*, *ammonia*, and *ammonium sulphide* precipitate from solutions of zirconium salts a white, flocculent hydroxide, which is insoluble in an excess of the precipitant, even of caustic soda and potash (difference from aluminium and beryllium), and is also not dissolved by boiling solution of ammonium chloride (difference from beryllium). Tartaric acid prevents the precipitation by alkalies. *Carbonates of potassium*, *sodium*, and *ammonium* gradually throw down basic zirconium carbonate as a white, flocculent precipitate, which redissolves in a large excess of potassium carbonate, more readily in potassium bicarbonate.

and most easily in ammonium carbonate (difference from aluminium). From the latter solution, a gelatinous hydroxide is precipitated by boiling. *Oxalic acid* precipitates fine, crystalline zirconium oxalate (difference from aluminium and beryllium), which is soluble in excess of oxalic acid, especially upon warming, and in hydrochloric acid as well as in an excess of ammonium oxalate solution even in the cold (difference from thorium). The solution is completely precipitated again by ammonia. A concentrated solution of *potassium sulphate* soon yields a white precipitate of potassium zirconium sulphate, which is insoluble in an excess of the reagent (difference from aluminium and beryllium), and which, if precipitated cold, dissolves readily in a large proportion of hydrochloric acid, but is almost absolutely insoluble in water and in hydrochloric acid if precipitated hot (difference from thorium and cerium). *Barium carbonate* does not precipitate zirconium completely, even upon boiling. *Hydrofluoric acid* does not precipitate zirconium solutions (difference from thorium and yttrium). *Sodium thiosulphate* precipitates zirconium salts upon boiling (difference from yttrium and didymium). The separation of the zirconium thiosulphate takes place on boiling even in the presence of 100 parts of water to 1 part of the oxide (important in regard to the complete separation from cerium). A concentrated solution of *hydrogen peroxide* precipitates from solutions of zirconium salts all the zirconium in the form of a white, voluminous precipitate, a hydrate of zirconium pentoxide, Zr_2O_5. The precipitate is insoluble in 1 per cent sulphuric acid, and also in dilute acetic acid. By boiling with acids, it is partly dissolved with decomposition (BAILEY). (Means of separating zirconium from titanic acid, niobic acid, ferric oxide, alumina, but not from thoria.) From neutral or very weakly acid solutions, an *alkali-metal iodate* precipitates zirconium completely as zirconium iodate. Heating facilitates the precipitation (TH. DAVIS, Jr.). (Means of separating zirconium from aluminium.) *Turmeric-paper* dipped into zirconium solutions slightly acidified with hydrochloric or sulphuric acid acquires a brownish-red color after drying (difference from the other earths). In the presence of titanic acid, which also has the effect of turning turmeric-paper brown, first treat the acid solution with zinc to reduce the titanic acid to titanic oxide, the solution of which does not affect turmeric-paper (PISANI). In relation to the microchemical detection of zirconium, see HAUSHOFER, p. 156, and BEHRENS, Zeitschr. f. analyt. Chem., 30, 156.

§ 112.

YTTRIUM, Y. (*Yttria*, Y_2O_3.)

Yttrium is a rare metal found in gadolinite, orthite, yttro-tantalite, and fergusonite. Yttria when pure is white, and when ignited in the oxidizing flame, it emits a white light without fusing or volatilizing. In nitric, hydrochloric, and dilute sulphuric acids, it is difficultly soluble in the cold, but on warming, it dissolves completely after some time (BAHR and BUNSEN). The solutions and likewise the salts of yttrium are colorless, and have an acid

reaction and a sweetish, astringent taste. Yttrium under no circumstances yields a direct spectrum, nor do the solutions of its salts show any absorption-bands (BAHR and BUNSEN). However, when strongly ignited, yttria shows a phosphorescence spectrum (CROOKES). Anhydrous yttrium chloride is not volatile (difference from aluminium, beryllium, and zirconium). *Potassium hydroxide* precipitates the white hydroxide, which is insoluble in an excess of the precipitant (difference from aluminium and beryllium). *Ammonia* and *ammonium sulphide* give the same reaction. *Alkali carbonates* produce a white precipitate, which dissolves with difficulty in potassium carbonate, but more readily in hydrogen potassium carbonate and in ammonium carbonate, though by no means so readily as the corresponding beryllium precipitate. On boiling, the solution of the pure hydroxide in ammonium carbonate deposits the whole of the yttrium; and if ammonium chloride is present at the same time, this is decomposed upon continued heating, with separation of ammonia, the precipitate redissolving as yttrium chloride. Saturated solutions of yttrium carbonate in ammonium carbonate have a tendency to deposit yttrium carbonate, which should be borne in mind. *Oxalic acid* produces a white precipitate (difference from aluminium and beryllium). The precipitate does not dissolve in oxalic acid, it dissolves with difficulty in dilute hydrochloric acid, and is partially dissolved by boiling with ammonium oxalate, but by diluting and cooling, the oxalate separates again almost completely (difference from thorium). *Potassium yttrium sulphate* dissolves readily in water and in solution of potassium sulphate (difference from thorium, zirconium, and the metals of cerite). *Barium carbonate* produces no precipitate in the cold (difference from aluminium, thorium, cerium, lanthanum, and didymium), and even on boiling, the precipitation is incomplete. *Turmeric-paper* is not altered by acidified solutions of yttrium salts (difference from zirconium). *Tartaric acid* does not interfere with the precipitation of yttrium by alkalies (characteristic difference between yttrium and aluminium, beryllium, thorium, and zirconium). The precipitate is yttrium tartrate. The precipitation ensues only after some time, but it is complete. *Sodium thiosulphate* does not precipitate yttrium (difference from aluminium, thorium, zirconium, and titanium). *Hydrofluoric acid* produces a precipitate (here yttrium differs from aluminium, beryllium, zirconium, and titanium) which is gelatinous, insoluble in water and hydrofluoric acid; before ignition, it will dissolve in mineral acids, but after ignition it is decomposed only by strong sulphuric acid. Yttrium gives clear, colorless beads with *borax* and *sodium metaphosphate*, in both the outer and inner flames (difference from cerium and didymium). In relation to the microchemical detection of yttrium, see HAUSHOFER, p. 148, and BEHRENS, Zeitschr. f. analyt. Chem., 30, 145.

Besides yttrium, there occur in gadolinite, etc., a number of similar elements, such as erbium, terbium, ytterbium, scandium, thulium, decipium, philippium, etc. (see § 117).

§ 113.

5. CERIUM, Ce. (*Oxides; Cerous*, Ce_2O_3, and *Ceric*, CeO_2.)

Cerium occurs sparingly in nature, principally as cerous silicate in cerite and orthite, as cerous phosphate in monazite, and in combination with fluorine in fluocerite. It combines with oxygen in two proportions, forming cerous oxide, Ce_2O_3, and ceric oxide, CeO_2, called also cerium dioxide and peroxide. Cerous oxide, which is obtained by igniting either ceric oxide or cerous carbonate or oxalate in a stream of hydrogen, is a white or bluish-gray powder. It absorbs oxygen rapidly from the air, and by ignition in the same is changed into ceric oxide. The cerous salts are white or colorless, and some of them are soluble in water. The solutions are colorless, have a sweet, astringent taste, and show no absorption-spectrum. Cerous chloride, $CeCl_3$, easily obtained by heating cerous oxide in carbon tetrachloride vapor (L. MEYER and R. WILKENS), is white, fusible, and not volatile (difference between cerium and aluminium, beryllium and zirconium). It is soluble in water. By boiling a solution of cerous sulphate, a salt is precipitated, which dissolves again upon cooling. Cerite (hydrous cerous silicate) is decomposed by fusion with sodium carbonate, and concentrated sulphuric acid also decomposes it. *Potassium hydroxide* precipitates white cerous hydroxide, which turns yellow in the air from the absorption of oxygen, and does not dissolve in an excess of the precipitant (difference from aluminium and beryllium). *Ammonia* precipitates basic salts, which are insoluble in an excess of the precipitant. Tartaric acid prevents the precipitation (difference from yttria). *Ammonium carbonate* precipitates white cerous carbonate, which is at first amorphous, but gradually becomes crystalline, and dissolves to some extent in an excess of the precipitant. *Oxalic acid* precipitates white cerous oxalate, which is amorphous at first, but gradually becomes crystalline. The precipitation is complete, even from moderately acid solutions (difference from aluminium and beryllium). The precipitate does not dissolve in oxalic acid, but it does dissolve in a very large quantity of hydrochloric acid, and to a slight extent in a boiling, concentrated solution of ammonium oxalate. In the last case, it separates out almost completely again upon diluting and cooling (difference from thorium). Even from somewhat acid solutions, a saturated solution of *potassium sulphate* precipitates white potassium cerous sulphate (difference from aluminium and beryllium), which is difficultly soluble in cold water, more readily in hot water (BAHR), and altogether insoluble in a saturated solution of potassium sulphate (difference from yttrium). The precipitate may be dissolved by boiling with a large quantity of water, to which some hydrochloric acid has been added. *Barium carbonate* does not produce a precipitate in the cold, but precipitates cerous salts completely upon heating. *Sodium thiosulphate* does not precipitate cerium, even on boiling with very concentrated solutions. The precipitated sulphur only carries down traces of the salt with it. From

solutions of cerous salts, *alkali-metal hypochlorites* precipitate bright yellow ceric hydroxide. If a cerous salt is dissolved in nitric acid with the addition of an equal volume of water, a small amount of *lead peroxide* is added, and the solution is then boiled for a few minutes, the liquid assumes a yellow color in consequence of the formation of a ceric salt, even if only a small amount of cerium is present. On evaporating this solution to dryness, heating the residue till a portion of the acid escapes, and treating it with water acidified with nitric acid, no cerium will be dissolved, but any didymium and lanthanum present will be dissolved (GIBBS). If potassium or sodium hydroxide is added to the solution of a cerous salt to distinct alkaline reaction (after having evaporated off any free, volatile acid, if such is present in large quantity), the solution evaporated to dryness, and a solution of *strychnine* in concentrated sulphuric acid (about 1 : 1000) poured over this residue, a magnificent bluish-violet liquid results, the color of which soon changes into red (PLUGGE).

Ceric oxide, obtained by igniting cerous hydroxide, carbonate, or oxalate in the air, or by heating cerous nitrate, forms a powder of an orange-yellow color when hot, but yellowish-white when cold. It is soluble in concentrated sulphuric acid upon heating, usually with the evolution of oxygen, to a yellow solution containing ceric and cerous sulphates. Nitric or hydrochloric acids scarcely dissolve it upon heating, but the latter acid dissolves it easily when potassium iodide is added, forming cerous chloride, $CeCl_3$, with the liberation of iodine, or also when alcohol or hydrogen peroxide is added to the acid. Ceric hydroxide is soluble in nitric and sulphuric acids. Hydrochloric acid dissolves it, with evolution of chlorine and formation of cerous chloride. The ceric salts are yellow or red, and their solutions are yellow. *Sulphurous acid* decolorizes the solutions, producing cerous salts. Solutions of ceric salts are precipitated slowly but completely by *barium carbonate* in the cold. *Sodium thiosulphate* precipitates a solution of ceric nitrate.

In the outer flame, *borax* and *sodium metaphosphate* dissolve cerium oxides to yellowish-red beads (difference from the preceding earth metals). The coloration gets fainter on cooling, and often disappears altogether. In the inner flame, colorless beads are obtained.

§ 114.

6. LANTHANUM, La. (*Oxide*, La_2O_3.)

This element is generally found associated with cerium. Lanthanum oxide is white, and remains unaltered by ignition in the air (difference from cerous oxide). In contact with cold water, it is slowly converted into a milk-white hydroxide; while with hot water, the conversion is rapid. The oxide and hydroxide change the color of reddened litmus-paper to blue, and they dissolve in boiling solution of ammonium chloride, as well as in dilute acids. In this, lanthanum oxide resembles magnesia. The salts of lan-

thanum are colorless. The saturated solution of lanthanum sulphate in cold water deposits a portion of the salt even at 30° (difference from cerium). *Potassium sulphate*, *oxalic acid*, and *ammonium oxalate* (acting upon lanthanum oxalate) give the same reactions as with cerous salts. *Potassium hydroxide* precipitates the hydroxide, which is insoluble in an excess of the precipitant, and does not turn brown in the air. *Ammonia* precipitates basic salts, which pass milky through the filter on washing. The precipitate produced by ammonium carbonate is entirely insoluble in an excess of the precipitant (difference from cerous salts). If a cold, dilute solution of lanthanum acetate is supersaturated with ammonia, the slimy precipitate repeatedly washed with cold water, and a little *iodine* in powder added, a blue coloration makes its appearance, which gradually pervades the entire mixture (characteristic difference between lanthanum and the other earth metals). *Barium carbonate* precipitates solutions of lanthanum salts completely, even in the cold.

§ 115.

7. Didymium, Di. (*Oxide*, Di_2O_3.)

This element, like lanthanum and in conjunction with it, is found associated with cerium. After intense ignition, didymium oxide appears white; but when moistened with nitric acid and feebly ignited, a dark brown peroxide is formed, which after intense ignition is converted into the white oxide. In contact with water, the oxide is slowly converted into hydroxide; it rapidly attracts carbon dioxide; its reaction is not alkaline; it dissolves readily in acids and also in a boiling solution of ammonium chloride. The salts soluble in water and their concentrated solutions have a reddish or a faint violet color. On heating, the nitrate is first converted into a basic salt (difference from lanthanum), which is gray when hot and also when cold. The chloride is not volatile. The saturated solution of the sulphate deposits salt, not at 30°, but upon boiling. *Potassium hydroxide* precipitates the hydroxide, which is insoluble in an excess of the precipitant, and does not alter in the air. *Ammonia* precipitates a basic salt, which is insoluble in ammonia, but somewhat soluble in ammonium chloride. *Alkali carbonates* produce a copious precipitate, which is insoluble in an excess of the precipitant, even in an excess of ammonium carbonate (difference from cerous salts), but dissolves slightly in concentrated solution of ammonium chloride. Tartaric acid prevents the precipitation by the alkalies. *Oxalic acid* precipitates salts of didymium almost completely. The precipitate is difficultly soluble in cold hydrochloric acid, but dissolves upon application of heat. It behaves towards ammonium oxalate like cerous oxalate. *Barium carbonate* precipitates didymium solutions slowly but completely. A concentrated solution of *potassium sulphate* precipitates didymium solutions more slowly and less completely than cerous solutions. The precipitate (potassium didymium sulphate) is insoluble in solution of potassium sulphate and in water (Delafontaine), but it dis-

solves in hot hydrochloric acid, although with difficulty. *Sodium thiosulphate* does not precipitate solutions of didymium. DIDYMIUM PEROXIDE is brown, soluble in hydrochloric acid, with evolution of chlorine, and in oxygen acids, with evolution of oxygen. With *borax*, in both flames, didymium oxide gives a nearly colorless bead, which in the presence of large quantities has a faint amethyst-red tinge. *Sodium metaphosphate* dissolves the oxide in the oxidizing flame to an amethyst-red bead inclining to violet. The color disappears in the reducing flame. With *sodium carbonate* in the outer flame, a grayish-white mass is obtained (difference from manganese). The *absorption-spectrum* given by the solutions of the salts is peculiarly characteristic for didymium. This was first described by GLADSTONE, and afterwards by O. L. ERDMANN and DELAFONTAINE. BAHR and BUNSEN have laid down the exact position of the bands (Zeitschr. f. analyt. Chem., 5, 110).

APPENDIX TO §§ 112–115.

§ 116.

Regarding the microscopic detection of cerium, lanthanum, and didymium, see HAUSHOFER, p. 40, and BEHRENS, Zeitschr. f. analyt. Chem., 30, 144.

For separating the metals under consideration, one of the following methods may be used: *a.* Neutralize the solution of the three bases almost completely, if it is acid, without, however, allowing a permanent precipitate to form; add a sufficient amount of sodium acetate and an excess of sodium hypochlorite, and boil for some time; cerium is thus precipitated—as ceric hydroxide (POPP), or as basic acetate which should be washed with sodium acetate (ERK)—while lanthanum and didymium remain in solution (POPP, Ann. Chem. Pharm., 131, 360). *b.* Precipitate the bases with potassium hydroxide, suspend the washed precipitate in potassium hydroxide solution, and pass in chlorine. Lanthanum and didymium oxides dissolve, while ceric oxide remains behind (DAMOUR and ST. CLAIRE DEVILLE, Compt. rend., 59, 272). *c.* Evaporate the solution of the nitrates to dryness, and heat the residue until the brown mass has become light yellow. If, after cooling, this is treated with boiling, dilute nitric acid, lanthanum and didymium go into solution, while cerium remains almost completely undissolved as basic nitrate (ROBINSON). *d.* Dissolve in an excess of strong nitric acid, boil with lead peroxide, evaporate the orange-yellow solution to dryness, and heat the residue until a part of its acid has been removed, treat with water which is acidified with nitric acid, and separate the undissolved basic ceric nitrate from the solution containing all the lanthanum and didymium (GIBBS, Zeitschr. f. analyt. Chem., 3, 396). In using the last method, it must be remembered that in the further treatment of the solution and the residue, lead is to be first removed by hydrogen sulphide. *e.* Heat the chromates to 110° and extract with hot water the lanthanum and didymium compounds, which remain undecom-

posed. Cerium remains behind as insoluble dioxide (PATTINSON and CLARK, Chem. News, **16**, 259).

From the solution of lanthanum and didymium obtained by one or the other of the foregoing methods, the bases are precipitated with ammonium oxalate, the oxalates are ignited, and the oxides thus obtained are treated with dilute nitric acid. If the separation of cerium was incomplete, the remainder of the cerium will be left behind. The solution is evaporated to dryness in a dish with a flat bottom, and heated to 400° or 500°. The salts fuse, and nitrous fumes escape. The residue is treated with hot water, which dissolves the lanthanum, leaving behind gray basic didymium nitrate. By many repetitions of the evaporation, etc., the two bases may be satisfactorily separated (DAMOUR and ST. CLAIRE DEVILLE). MOSANDER recommends converting the didymium and lanthanum into sulphates, making a saturated solution of the dry salts in water at 5° or 6°, and heating the solution to 30°, when the lanthanum sulphate is for the most part thrown down, and the didymium sulphate is mostly held in solution. For other methods of separating lanthanum and didymium, compare CL. WINKLER, Zeitschr. f. analyt. Chem., **4**, 417; ZSCHIESCHE, *ibid.*, **9**, 541; FRERICHS, *ibid.*, **13**, 217.

ADDENDA TO §§ 109–116.

§ 117.

The chemistry of the rare-earth metals has recently been studied by many investigators,* and the views which were held concerning them at the time of the appearance of the 15th (German) edition of this book have been considerably modified. It has been found that a number of the bodies which were previously thought to be elements are mixtures of several, or even of many, very similar elements. According to CROOKES, yttrium consists of a complex of five, or, more probably, of eight, distinct elements. Didymium contains two elements. An actual separation of all these bodies has not, as yet, been accomplished, at least completely, although evidence has been obtained in regard to their diversity in spectroscopic properties and atomic weight.

In addition to the elements just considered, a large number of others belonging to the rare-earth metals are to be mentioned; as erbium, terbium, ytterbium, scandium, thulium, decipium, philippium, samarium, holmium, mosandrium, dysprosium, austrium, gadolinium, neodymium, and praseodymium.

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* The following should receive special mention here: CROOKES, AUER V. WELSBACH, LECOQ DE BOISBAUDRAN, KRÜSS, NILSON, RAMMELSBERG, BETTENDORF, SCHOTTLÄNDER, BRAUNER, LAWRENCE SMITH, DIDIER, CLÈVE, DEMARÇAY, BECQUEREL, THOMPSON, and BLOMSTRAND.

Since the study of these elements cannot yet be considered as finished, and an exact characterization of many of them is not yet possible, I cannot attempt to give their behavior and reactions, and have therefore treated the complex yttrium and didymium as simple metals.

§ 118.

8. Titanium, Ti.

Titanium forms three oxides; titanious oxide, TiO (only known in the form of the hydroxide), titanic oxide, Ti_2O_3, and titanic acid (anhydride), TiO_2. The latter is more frequently met with in analysis. Titanic acid is found in the free state in rutile,* brookite, and anatase, and in combination with bases in titanite, titaniferous iron, etc. It also occurs in small proportions in bauxites, in many iron ores, in clays, and generally in silicates, consequently also in cast-iron and in blast-furnace slags. The small, copper-colored cubes which are occasionally found in such slags consist of a combination of titanium cyanide with titanium nitride. Feebly ignited titanic acid is white, but it transiently acquires a lemon tint when heated. According to the manner of preparation, very intense ignition may give it a yellowish-white color, or if it previously contained ammonium chloride, a brownish color, due to the formation of titanium nitride (v. d. Pfordten). It is infusible, insoluble in water, and its specific gravity is 3.9 to 4.25. When strongly ignited in hydrogen for a long time, it is converted into the indigo-blue compound, Ti_7O_{12}, which is to be considered as a combination of titanic acid with titanic oxide (v. d. Pfordten†). Titanium tetrachloride, $TiCl_4$, is a colorless, volatile liquid, which fumes strongly in the air, and decomposes very violently with water. Alcohol dissolves it more quietly to a clear fluid, which also remains clear upon mixing it with water. Upon the addition of ether, the alcoholic solution which has been diluted with water becomes yellow. Upon mixing titanium tetrachloride with concentrated hydrochloric acid, a yellow compound is formed, while much heat is produced and hydrogen chloride is given off. This compound dissolves in an excess of hydrochloric acid to a clear, bright yellow liquid, which does not fume, and can be diluted with water as much as desired without becoming turbid (v. d. Pfordten).

a. Deportment with Acids, and Reactions of Acid Solutions of Titanic Acid.—Ignited titanic acid is insoluble in acids, except in hydrofluoric and concentrated sulphuric acids. If the solution in hydrofluoric acid is evaporated with sulphuric acid, no titanium tetrafluoride will volatilize (difference from silicic acid). When evaporated with hydrofluoric

* Concerning the preparation of pure titanic acid from rutile, the most important compounds of titanium, and the reactions of the solutions of the three titanium oxides, compare v. d. Pfordten, Ann. d. Chem., **234**, 257, *et seq.*, and especially **237**, 201, *et seq.*

† Ann. d. Chem., **237**, 230.

acid alone, titanic acid is volatilized. Upon sufficiently long-continued fusion with potassium disulphate, titanic acid gives a clear mass, which is completely soluble in a large proportion of cold or lukewarm water. Titanic acid is very easily brought into a clear solution by fusing with hydrogen potassium fluoride, and dissolving the fusion in dilute hydrochloric acid. Potassium titanium fluoride is difficultly soluble in water, 1 part requiring 96 parts at 14°. Both when moist and when it has been dried without the aid of heat, hydrated titanic acid is soluble in dilute acids, especially in hydrochloric and in sulphuric acids. All solutions of titanic acid in hydrochloric or sulphuric acids, especially the latter, and consequently also solutions obtained by treating acid potassium sulphate fusions with water, when subjected in a highly dilute state to *long-continued boiling*, deposit metatitanic acid as a white powder, insoluble in dilute acids. Presence of much free acid retards the separation and diminishes the quantity of the precipitate. The precipitation is most complete when the mass obtained by fusion with potassium disulphate is dissolved with the addition of some sulphuric acid, the solution neutralized with potassium hydroxide, and then, after the addition of .5 g of sulphuric acid for each 100 cc of liquid, it is boiled for six hours with renewal of the water lost by evaporation (LÉVY). The precipitate which separates from hydrochloric acid solutions may be filtered, but it will pass milky through the filter on washing, unless an acid or ammonium chloride is added to the washing water. From solutions of titanic acid in hydrochloric or sulphuric acid, solution of *potassium hydroxide* throws down titanic acid as a bulky, white precipitate, which is insoluble in an excess of the precipitant; *ammonia*, *ammonium sulphide*, and *barium carbonate* act in the same way. The precipitate, thrown down cold and washed with cold water, is soluble in hydrochloric and in dilute sulphuric acids, and presence of tartaric acid prevents its formation. In acid solutions of titanic acid, *potassium ferrocyanide* produces a bright reddish-yellow precipitate; *potassium ferricyanide*, a yellow; and *infusion of galls*, a brownish precipitate, which speedily turns orange-red. On boiling a solution of titanic acid with *sodium thiosulphate*, all the titanic acid is thrown down. *Sodium phosphate* throws it down almost completely as phosphotitanic acid, even from solutions containing much hydrochloric acid. The washed precipitate consists of $P_2Ti_2O_9$ (MERZ). Titanic acid is also precipitated by *sodium phosphate* in the presence of a large excess of *formic acid;* also by boiling with much *sodium acetate* and *acetic acid*. Both methods of precipitation, especially the latter, accomplish a complete separation from alumina if the operation is repeated (GOOCH*). *Hydrogen peroxide* colors titanic acid solutions orange-yellow (SCHÖN). [The solution used for this test should contain no fluorides.] When the colored solution is shaken with ether, the colored substance does not go into that solvent (HEPPE). Stannous chloride or zinc dust decolorize the solution. The reaction is not applicable in the presence of vanadic, molybdic, and chromic

* Chem. Centralbl., 1887, p. 153.

acids, nor in the presence of large amounts of ferric salts. [When iron is present, a solution in sulphuric acid should be used for the test, because ferric sulphate gives far less color than ferric chloride. The reaction in this case is delicate, even in the presence of a large amount of iron.] The yellow solution which is obtained by the action of aqueous sulphurous acid upon granulated zinc (*hydrosulphurous acid*, according to SCHÜTZENBERGER; *hyposulphurous acid*, $H_2S_2O_4$, according to BERNTHSEN) produces a red coloration in titanic acid solutions, even when extremely dilute. The red coloring matter is not taken up by ether when the solution is shaken with that liquid (R. FRESENIUS). *Metallic zinc* or *tin* produces, after some time, a pale violet to bluish coloration of the solution, in consequence of the reduction of titanic acid to titanic oxide. Subsequently, a blue precipitate separates, which gradually becomes white. If potassium hydroxide or ammonia is added to the solution which has become blue but is still clear, blue titanic hydroxide separates, which, by the decomposition of water, gradually changes into white, hydrated titanic acid. The reduction of titanic acid in hydrochloric solution takes place also in the presence of potassium fluoride (difference from niobic acid), the fluid in this case becoming light green. The solutions of titanium tetrachloride in water have properties which vary according to their preparation. If, for example, the chloride is dissolved in water in such a manner that no heating takes place, a slightly opalescent liquid is obtained, which is only slightly clouded by boiling (titanium tetrachloride solution),, while the same solution, if kept for a few weeks, gives a large precipitate by boiling (metatitanic acid solution). The solutions are also distinguished by the fact that the first remains clear upon the addition of sulphuric or oxalic acids, while the other is precipitated by each of these. If the mass obtained by fusing titanic acid with potassium disulphate is dissolved in cold water, a precipitation is made with ammonia, the precipitate is washed with cold water and dissolved in as little hydrochloric acid as possible, a solution of metatitanic acid is obtained; *i.e.*, it is precipitated by boiling as well as by sulphuric and oxalic acids.*

b. Reaction with Alkalies.—Recently precipitated titanic acid is almost absolutely insoluble in solution of potassium hydroxide. If titanic acid is fused with *potassium hydroxide* and the mass treated with water, the solution contains a little more titanic acid. By fusion with *alkali carbonates*, normal alkali titanates are formed, with expulsion of carbon dioxide. From the fused mass, cold water extracts alkali and alkali carbonate, leaving behind acid titanate of the alkali metal, soluble in hydrochloric acid with the production of a clear solution or the formation of a precipitate, according to the concentration of the acid. When hydro-

* The statements concerning the formation and properties of titanic chloride solutions and metatitanic chloride solutions, by R. WEBER, Pogg. Ann., 120, 287, and C. RAMMELSBERG, Berlin Monatsber., 1874, p. 490, and Zeitschr. f. analyt. Chem., 13, 447, differ from each other. This subject, therefore, needs a new investigation.

chloric acid of about 36 per cent is used, titanic acid separates in a gelatinous form (H. ROSE, v. D. PFORDTEN).

When titanic acid is mixed with charcoal and ignited in a *stream of chlorine*, or is exposed to the vapor of carbon tetrachloride below a red heat (DEMARÇAY), it gives titanium tetrachloride as a volatile liquid, which emits copious fumes in the air (see above). At the point of the outer blowpipe flame, *sodium metaphosphate* dissolves titanic acid to a colorless bead, but with difficulty; while in the outer flame, yet near the point of the inner flame, it dissolves readily and in considerable quantity. If the clear and colorless bead is again held in the point of the outer flame, it becomes opaque if sufficiently saturated, and by continued action of the flame, titanic acid will separate in microscopic crystals of the form of anatase (G. ROSE). According to A. KNOP, the crystals are a compound of titanic and phosphoric acids; according to G. WUNDER, they are composed of sodium phosphate and titanate, and are rhombohedral. If the bead is held in a good reducing flame for some time, it will appear yellow while hot, red while cooling, and violet when cold. The reduction is promoted by the addition of a little tin. If some ferrous sulphate is added, the bead obtained in the reducing flame will appear blood-red. If a substance containing titanium is fused upon the loop of a fine platinum wire with a little *sodium carbonate*, in the inner flame of a BUNSEN burner, which is made somewhat luminous, and is heated until all the sodium carbonate has volatilized, there is formed the copper-red compound composed of titanium cyanide and nitride, $3Ti_2N_2.TiC_2N_2$, in consequence of the action of the *cyanogen* contained in the gas (LÜDEKING). In order to detect titanium in minerals, .1 g of the finely pulverized substance is fused with .2 g of sodium fluoride and 3 g of acid sodium sulphate. By treating the mass with cold water, the titanic acid is obtained in solution, in which it can be detected (A. NOYES). In regard to the microscopic detection of titanium, compare HAUSHOFER, p. 130; BEHRENS, Zeitschr. f. analyt. Chem., **30**, 156.

§ 119.

9. TANTALUM, Ta.

With oxygen, tantalum forms tantalous oxide, TaO_2, and tantalic acid (anhydride), Ta_2O_5. Tantalum occurs in columbite and tantalite (almost always in conjunction with niobium). Tantalic acid is white, and is only pale yellowish when hot. When separated in the wet way, the acid contains hydroxyl-water. The water-free acid has a specific gravity of 7.0 to 8.25. Tantalic acid is not reduced by ignition in a current of *hydrogen*. It combines with acids as well as with bases.

a. Acid Solutions.—When tantalic acid is intimately mixed with charcoal and ignited in a current of dry *chlorine*, and also by the action of carbon tetrachloride vapors below a red heat (DEMARÇAY), tantalum chloride,

$TaCl_5$, is formed. The latter is yellow, solid, fusible, and can be sublimed, and is completely decomposed by water, with separation of tantalic acid (hydroxide). The chloride is entirely soluble in sulphuric acid, nearly so in hydrochloric acid, and partially soluble in potassium hydroxide solution. If titanium is present, on treating the mixtures of oxides and charcoal with a current of chlorine, titanium chloride will be formed, which fumes strongly in the air. Hydrated tantalic acid dissolves in *hydrofluoric acid;* and the solution, when mixed with potassium fluoride, yields a very characteristic salt in fine needles, $2KF.TaF_5$, which is distinguished by its difficult solubility in water acidified with hydrofluoric acid (1 part of the acid to 150 or 200 of water). (Distinction and method of separation from niobium.) Hydrochloric and concentrated sulphuric acids do not dissolve ignited tantalic acid. With potassium disulphate, it fuses to a colorless mass; and if this is treated with water, tantalic acid combined with sulphuric acid remains undissolved (difference between tantalic acid and titanic acid, but it cannot be made the ground of a method of separation). When ignited in an atmosphere of ammonium carbonate, the tantalic sulphate is converted into tantalic acid. If a solution of alkali tantalate is mixed with hydrochloric acid in excess, the precipitate first formed redissolves to an opalescent fluid. From this liquid, *ammonia* and *ammonium sulphide* precipitate tantalic acid or an acid ammonium tantalate, but tartaric acid prevents the precipitation. *Sulphuric acid* precipitates tantalic sulphate from the opalescent fluid. When acid solutions of tantalic acid are brought into contact with *zinc*, no blue coloration is observed (difference between tantalic acid and niobic acid).

b. Behavior to Alkalies.—By continued fusion with *potassium hydroxide*, potassium tantalate is formed, and the fused mass will dissolve in water. By fusion with *sodium hydroxide*, a turbid mass is obtained, and a little water poured on this will dissolve out the excess of sodium hydroxide, leaving the whole of the sodium tantalate undissolved. The latter salt is insoluble in solution of caustic soda, but the sodium tantalate will dissolve in water after the removal of the excess of soda. Solution of sodium hydroxide throws down from this solution the sodium tantalate, and if the precipitant is added slowly, the form of the precipitate is crystalline. From solutions of alkali tantalates, carbon dioxide throws down acid salts not soluble in boiling solution of sodium carbonate, and even from the dilute solutions, *sulphuric acid* throws down tantalic sulphate. *Potassium ferrocyanide* and *infusion of galls* produce precipitates only in acidified solutions, the precipitate produced by the former being yellow, and by the latter, light brown.

Sodium metaphosphate dissolves tantalic acid to a colorless bead, which is colorless also when hot, remains colorless even in the inner flame, and does not acquire a blood-red tint by addition of ferrous sulphate (difference between tantalum and titanium). The microscopic detection of tantalum is based upon the observation of the crystals, in which potassium tantalum fluoride and sodium tantalate can be obtained (BEHRENS, Zeitschr. f. analyt. Chem., 30, 162; HAUSHOFER, p. 105).

§ 120.

10. Niobium, Nb, or Columbium, Cb.

Niobium combines with oxygen in several proportions, viz., NbO, NbO_2, and Nb_2O_5. It is rare, being found in columbite, samarskite, etc., and it is usually accompanied by tantalum. Niobic acid (anhydride). Nb_2O_5, is white, can be obtained in a crystallized condition (Ebelmen, A. Knop), and turns transiently yellow when ignited (difference from tantalic acid). Its specific gravity lies between 4.37 and 4.53 (difference from tantalic acid). By strong ignition in *hydrogen*, the niobic acid is converted into black NbO_2. Niobic acid combines both with bases and with acids.

a. Acid Solutions of Niobic Acid.—Concentrated *sulphuric acid* dissolves the acid on heating, unless it has been too strongly ignited. On the addition of much cold water, a clear solution is obtained. On fusing with *potassium disulphate*, it dissolves readily to a colorless mass, and on treating the fusion with boiling water, niobic acid containing sulphuric acid remains undissolved, but is readily soluble in hydrofluoric acid (see below). By mixing niobic oxide intimately with charcoal and treating with a current of *chlorine*, and also by heating it in the vapor of carbon tetrachloride at about 440° (Demarçay), a mixture is obtained of white, infusible, difficultly volatile niobic oxychloride, $NbOCl_3$, and yellow more volatile niobic chloride, $NbCl_5$. Treated with water, both compounds give turbid fluids, in which a part of the niobium is separated as niobic acid, but the larger portion remains dissolved. By boiling with hydrochloric acid and afterwards adding water, the compounds give clear solutions, which are not precipitated by boiling or by sulphuric acid in the cold (difference from tantalum chloride). By igniting niobic oxide in the vapor of niobium chloride, the oxychloride is formed (difference from tantalic oxide). From the acid solutions of niobic acid, *ammonia* and *ammonium sulphide* throw down niobic acid containing ammonia, which, as well as any niobic acid that has not been ignited, dissolves in *hydrofluoric acid*. When mixed with potassium fluoride, the hydrofluoric solution gives potassium niobium fluoride, $2KF.NbF_5$, if hydrofluoric acid is in excess; otherwise it gives potassium niobium oxyfluoride, $2KF.NbOF_3$. The latter salt is also obtained when potassium niobate is dissolved in hydrofluoric acid; it is readily soluble in cold water, 1 part dissolving in 12.5 parts (difference from potassium titanium fluoride, which requires 96 parts of water, and from potassium tantalum fluoride, which requires 200 parts of water). If the solution of potassium niobium oxyfluoride is boiled for a long time, with renewal of the evaporated water, niobium dioxyfluoride separates in microscopic crystals (Krüss and Nilson*). If very dilute potassium hydroxide is added to a very dilute, boiling solution of niobic

* Jahresber. über die Fortschritte d. Chemie, 1887, p. 557.

acid in hydrofluoric acid until reddish litmus paper begins to change its color a little, and then ammonia is added to neutralization, all the niobic acid is precipitated (difference and means of separation from titanic acid, DEMARÇAY *). On digesting a hydrochloric or sulphuric acid solution of niobic acid with *zinc* or *tin*, it acquires a blue and generally also a brown color, in consequence of the reduction of the niobic acid to lower oxides. In the presence of alkali-metal fluorides, the reduction does not take place (difference from titanic acid).

b. Alkaline Solutions.—With *potassium hydroxide*, niobic acid fuses to a clear mass, soluble in water. To *sodium hydroxide*, niobic acid shows the same deportment as tantalic acid. From the solution of potassium niobate, *sodium hydroxide* precipitates an almost insoluble sodium niobate. On boiling a solution of potassium niobate with *hydrogen potassium carbonate*, an almost insoluble acid potassium niobate is thrown down. On fusing niobic acid with *sodium carbonate* and boiling the fusion with water, a crystalline acid sodium niobate remains undissolved. *Carbon dioxide* when passed into solution of sodium niobate precipitates all the niobic acid as an acid salt.

Sodium metaphosphate dissolves niobic acid readily. The bead held in the outer flame appears colorless as long as it is hot, but in the inner flame, it has a violet, blue, or brown color, according to the quantity of the acid present, and a red color on the addition of ferrous sulphate. The microscopic detection of niobium is accomplished by observing the crystals of sodium niobate (see HAUSHOFER, p. 104; BEHRENS, Zeitschr. f. analyt. Chem., 30, 161).

For the best methods of detecting several, or possibly all, of the members of the third group in presence of each other, see Part II, Section III.

§ 121.

FOURTH GROUP.

More common metals: ZINC, MANGANESE, NICKEL, COBALT, IRON.

Rarer elements: URANIUM, THALLIUM, INDIUM, GALLIUM, VANADIUM.

Properties of the Group.—If they contain a stronger free acid in sufficient amount, solutions of the metals of the fourth group are not precipitated at all by hydrogen sulphide, nor are neutral solutions—at least not completely. Alkaline solutions, however, are completely precipitated by hydrogen sul-

* Jahresber. über die Fortschritte d. Chemie, 1885, p. 1929.

phide; and so are other solutions, if a sulphide of an alkali metal is used as the precipitant instead of hydrogen sulphide.* The precipitates are hydrated sulphides corresponding to the oxides of the metals.† They are insoluble in water. Some of them are easily soluble in dilute acids, but others (nickel and cobalt sulphides) are very difficultly soluble. In alkali-metal sulphides, most of them are insoluble, while others are soluble, either slightly under certain circumstances (nickel), or even completely (vanadium).

The metals of the fourth group differ, accordingly, from those of the first and second groups in this, that their solutions are precipitated by ammonium sulphide; and from those of the third group, inasmuch as the precipitates produced by ammonium sulphide are sulphides, and not hydroxides, as is the case with aluminium, chromium, etc.

Special Reactions of the More Common Metals of the Fourth Group.

§ 122.

a. Zinc, Zn. (*Oxide*, ZnO.)

1. Metallic zinc is bluish-white and very bright. When exposed to the air, a thin coating of basic zinc carbonate forms gradually on its surface. It is of medium hardness, malleable at a temperature of between 100° and 150°, but otherwise more or less brittle. It fuses readily on charcoal before the blowpipe, boils afterwards, and burns with a bluish-green flame, giving off white fumes, and coating the charcoal support with oxide. Pure zinc scarcely dissolves in dilute hydrochloric and sulphuric acids; in very dilute nitric acid, it dissolves with evolution of nitrous oxide; and in more concentrated nitric acid, with evolution of nitric oxide. Impure

* Vanadic acid behaves in a very peculiar way with ammonium sulphide (see § 133).

† Alkali-metal sulphides precipitate a mixture of ferrous sulphide and sulphur, from solutions of ferric salts. It is only when a ferric salt solution is allowed to flow slowly into an excess of a sulphide solution that a hydrated sulphide corresponding to ferric oxide is obtained (Berzelius).

zinc, or zinc which is in contact with electro-negative metals, dissolves in dilute hydrochloric or sulphuric acid, with evolution of hydrogen gas.

2. ZINC OXIDE and ZINC HYDROXIDE are usually white powders, which are insoluble in water, but dissolve readily in hydrochloric, nitric, and sulphuric acids. Zinc oxide acquires a lemon-yellow tint when heated, but resumes its original, white color upon cooling. When ignited before the blowpipe, it glows with considerable brilliancy.

3. The ZINC SALTS are colorless or white if the acid causes no coloration. Part of them are soluble in water, and the rest in acids. The normal salts of zinc which are soluble in water redden litmus-paper, and those containing volatile oxygen acids are readily decomposed by heat, with the exception of zinc sulphate, which can bear a dull red heat without undergoing decomposition. Zinc chloride is volatile at a red heat.

4. From neutral solutions of zinc salts of strong acids, *hydrogen sulphide* precipitates a portion of the metal as white, hydrated ZINC SULPHIDE, ZnS. From solutions of neutral zinc salts of weak acids, however (*e.g.*, from zinc acetate solutions or from solutions of zinc salts of strong acids which contain normal salts of weak acids in sufficient amount, as sodium acetate, sodium formate, ammonium sulphocyanide), hydrogen sulphide precipitates all the zinc upon warming. In acid solutions, no precipitate is formed if the free acid present is one of the stronger ones, and if it is present in sufficient amount. Alkali-metal acid sulphates only prevent the precipitation when they are present in large amount. When they are present in smaller quantities, a part of the zinc is precipitated. From a sufficiently dilute solution of zinc in acetic acid, formic acid (DELFFS, HAMPE), monochloracetic acid (v. BERG), or succinic acid (ALT and J. SCHULZE), the zinc is also precipitated, even if the acid is in excess. Warming to 50° or 60° facilitates the precipitation.

5. From neutral solutions, *ammonium sulphide*, and from alkaline solutions, hydrogen sulphide, throw down the whole of the metal as hydrated ZINC SULPHIDE, in the form of a white precipitate. Ammonium chloride greatly promotes the separation of the precipitate, which from very dilute solutions sepa-

rates only after long standing. This precipitate is not dissolved by an excess of ammonium sulphide, nor by potassium hydroxide or ammonia; but it dissolves readily in hydrochloric, nitric, and dilute sulphuric acids. It is insoluble in acetic acid.

6. *Potassium* and *sodium hydroxides* throw down ZINC HYDROXIDE, $Zn(OH)_2$, in the form of a white, gelatinous precipitate, which is readily and completely redissolved by an excess of the precipitant. Upon boiling these alkaline solutions, they remain, if concentrated, unaltered; but from dilute solutions, nearly the whole of the zinc hydroxide separates as a white precipitate. Ammonium chloride, added to alkaline solutions containing only a very small excess of potassium or sodium hydroxides, produces a white precipitate of zinc hydroxide, which, however, redissolves on addition of more ammonium chloride. Solutions which contain larger amounts of potassium or sodium hydroxides are not precipitated by ammonium chloride (difference from aluminium).

7. In zinc solutions, if they do not contain a large excess of free acid, *ammonia* also produces a precipitate of ZINC HYDROXIDE, which readily dissolves in an excess of the precipitant. The concentrated solution turns turbid when mixed with water. On boiling the concentrated solution, a part of the zinc hydroxide separates, while on boiling the dilute solution, all of it precipitates. Ammonium salts interfere with or prevent these precipitations.

8. *Sodium carbonate* produces a precipitate of BASIC ZINC CARBONATE, which is insoluble in an excess of the precipitant. The composition of the precipitate varies according to the concentration and temperature of the solution and the excess of the precipitant. Presence of ammonium salts in great excess prevents the formation of this precipitate.

9. *Ammonium carbonate* also produces a precipitate of BASIC ZINC CARBONATE, but this redissolves upon further addition of the precipitant. On boiling the dilute solution, a white precipitate is produced. Ammonium salts hinder or prevent this precipitation.

N.B.—Non-volatile organic acids interfere more or less with the precipitation of solutions of zinc by the caustic and carbonated alkalies. Sugar does not prevent the precipitations.

10. In the cold, *barium carbonate* fails to precipitate solutions of zinc salts, with the exception of the sulphate.

11. *Potassium cyanide* precipitates white ZINC CYANIDE, $Zn(CN)_2$. This dissolves in an excess of the precipitant. If the excess of potassium cyanide is not too great, potassium sulphide or sodium sulphide precipitates hydrated zinc sulphide at once from this solution, while hydrogen sulphide or ammonium sulphide precipitates it slowly and incompletely.

12. *Potassium ferrocyanide* throws down ZINC FERROCYANIDE, $Zn_2Fe(CN)_6$, as a white, slimy precipitate, somewhat soluble in excess of the precipitant, but difficultly soluble in hydrochloric acid. It is formed even in a solution to which tartaric acid and an excess of ammonia have been added.

13. *Potassium ferricyanide* throws down ZINC FERRICYANIDE, $Zn_3Fe_2(CN)_{12}$, as a brownish orange-yellow precipitate, soluble in hydrochloric acid and in ammonia.

14. If a mixture of a zinc compound with *sodium carbonate* is exposed to the *reducing flame* of the blowpipe, the charcoal support becomes covered with a coating of ZINC OXIDE, which presents a yellow color while hot, and turns white upon cooling. This coating is produced by the reduced metallic zinc volatilizing at the moment of its reduction, and being reoxidized in passing through the outer flame. The METALLIC INCRUSTATION, obtained according to p. 35, is black, with a brown edge; but the INCRUSTATION OF OXIDE is white, and therefore invisible upon porcelain. They may be dissolved in a little nitric acid and examined according to 15.

15. If zinc oxide or one of the zinc salts is moistened with solution of *cobalt nitrate*, and then heated before the blowpipe, an unfused mass of a beautiful GREEN color is obtained, which is a compound of zinc oxide with cobalt oxide. If, therefore, in the first experiment described in 14, the coating on the charcoal is moistened with cobalt solution and ignited, it appears *green when cold*. This test may be applied with great delicacy by mixing the solution to be tested with a very little of the cobalt solution (not enough to give a bright red color), adding sodium carbonate in slight excess, boiling, filtering off, washing, and igniting on platinum foil. On triturating the residue, the green color may be distinctly and readily observed (BLOXAM).

16. In relation to the microscopic detection of zinc, see HAUSHOFER, p. 151; BEHRENS, Zeitschr. f. analyt. Chem., **30**, 142.

§ 123.

b. MANGANESE, Mn. (*Manganous Oxide*, MnO.)

1. METALLIC MANGANESE is whitish-gray, dull, very hard, brittle, and fuses with very great difficulty. It oxidizes rapidly in moist air, and in water with evolution of hydrogen, and crumbles to a dark green powder. It dissolves readily in acids, forming manganous salts.

2. MANGANOUS OXIDE is light green, and manganous hydroxide, $Mn(OH)_2$, is white. The former smoulders to brown mangano-manganic oxide, Mn_3O_4, when heated in the air; the latter, even at the ordinary temperature, rapidly absorbs oxygen from the air and passes into brown mangano-manganic hydroxide. Both are readily soluble in hydrochloric, nitric, and sulphuric acids. The brownish-black manganic oxide, Mn_2O_3, and the black manganese dioxide, MnO_2, dissolve to manganous chloride, with evolution of chlorine, when heated with hydrochloric acid; and to manganous sulphate, with evolution of oxygen, when heated with concentrated sulphuric acid.

3. The MANGANOUS SALTS are colorless or pale red if their acid produces no coloration. Part of them are soluble in water, and the rest in acids. The salts containing volatile oxygen acids are readily decomposed at a red heat, with the exception of the sulphate, which withstands a red heat without decomposition. The solutions do not alter vegetable colors.

4. *Hydrogen sulphide* does not precipitate acid solutions, even if the weaker acids, such as acetic, formic, monochloracetic, or succinic acids, are present. Neutral solutions, also, are not precipitated, or are precipitated very imperfectly.

5. From neutral solutions, *ammonium sulphide*, and from alkaline solutions, hydrogen sulphide, throw down the whole of the metal as hydrated MANGANOUS SULPHIDE, $MnS.H_2O$, in form of a light flesh-colored, or (with small quantities) yellowish-white precipitate, which acquires a dark brown color in

the air, on account of oxidation. This precipitate is insoluble in ammonium sulphide and in alkalies, but readily soluble in hydrochloric, nitric, and acetic acids. The separation of the precipitate is materially promoted by addition of a moderate amount of ammonium chloride. From very dilute solutions, the precipitate separates only after standing some time in a warm place. Ammonium oxalate, tartrate, but especially citrate, retard the precipitation, the latter salt also interfering with its completeness. In the presence of ammonia and ammonium sulphide in large excess, the flesh-colored hydrated precipitate occasionally passes into the green, crystalline sulphide, $3MnS.2H_2O$, even in the cold, the change being greatly facilitated by boiling, and being hindered more or less by the presence of ammonium chloride. Solutions containing much free ammonia should be nearly neutralized with hydrochloric acid before precipitating with ammonium sulphide.

6. *Potassium* and *sodium hydroxides* produce whitish precipitates of MANGANOUS HYDROXIDE, $Mn(OH)_2$, which upon exposure to the air speedily acquire a brownish and finally a deep blackish-brown color, owing to the conversion of the manganous hydroxide into mangano-manganic hydroxide by the absorption of oxygen from the air. *Ammonia* also precipitates manganous hydroxide, but the precipitate never contains more than about half the manganese present (compare the analogous behavior of magnesium salts). Ammonia and ammonium carbonate do not redissolve this precipitate; but presence of ammonium chloride in sufficient amount entirely prevents the precipitation by ammonia, and renders incomplete that by potassium and sodium hydroxides. Of precipitates already formed, solution of ammonium chloride redissolves only those parts which have not yet undergone oxidation. The solution of the manganous hydroxide in ammonium chloride is due to the tendency of the manganous salts to form double salts with ammonium salts. The ammoniacal solutions of these double salts turn brown in the air, and deposit dark brown mangano-manganic hydroxide. This dissolves in a solution of acid potassium oxalate to a beautiful red solution containing potassium manganic oxalate.

7. If *potassium* or *sodium hydroxide* or ammonia is added to a solution of a manganous salt, and a solution of *bromine* or of *hydrogen peroxide* is then added, all the manganese separates as brownish-black, hydrated MANGANESE DIOXIDE, $MnO_2.H_2O$. Heating facilitates the separation. Solutions of manganous salts containing *sodium acetate* are also precipitated by bromine upon heating.

N.B.—Non-volatile organic acids may interfere with or prevent the precipitation of manganous hydroxide or manganese dioxide. Sugar interferes with or prevents the precipitation as manganous hydroxide, but not as manganese dioxide.

8. *Ammonium carbonate* precipitates white MANGANOUS CARBONATE, $MnCO_3.H_2O$. After a considerable time, the precipitation is complete, even in presence of ammonium chloride. *Sodium* or *potassium carbonate* produces a white precipitate, which, according to circumstances, is HYDROUS MANGANOUS CARBONATE, MANGANOUS HYDROXIDE, or a MIXTURE OF BOTH. When freshly precipitated, this dissolves in ammonium chloride solution, but it is insoluble in an excess of the precipitant.

N.B.—Non-volatile organic acids hinder or prevent the precipitations by the fixed alkali carbonates. The precipitation by ammonium carbonate is retarded but not prevented by them.

9. *Potassium ferrocyanide* precipitates MANGANOUS FERROCYANIDE, $Mn_2Fe(CN)_6$, as a white precipitate, which is rather difficultly soluble in hydrochloric acid. The precipitation also occurs in a freshly prepared, ammoniacal solution of a manganous salt, which contains ammonium tartrate (difference from iron, L. BLUM).

10. *Potassium ferricyanide* precipitates MANGANOUS FERRICYANIDE, $Mn_3Fe_2(CN)_{12}$, as a brown precipitate, which is but slightly soluble in cold hydrochloric acid and insoluble in ammonia. By boiling with a large excess of concentrated hydrochloric acid, the precipitate dissolves with decomposition.

11. If a few drops of a fluid containing a manganous salt, and free from chlorine, are sprinkled on *lead dioxide*, and nitric acid free from chlorine is added, the mixture boiled and

allowed to settle, the fluid acquires a deep red color, from the formation of permanganic acid, $HMnO_4$* (HOPPE-SEYLER).

12. Upon digestion in the cold, *barium carbonate* does not precipitate aqueous solutions of manganous salts, with the exception of manganous sulphate.

13. If a manganese compound is treated with *phosphoric acid*, evaporated to syrupy consistence, and then (after the addition of a little potassium nitrate if a manganous compound is under experiment) it is heated more strongly, a violet mass is obtained, which is semi-liquid while hot and solid upon cooling, due to the formation of MANGANIC PHOSPHATE. This reaction is very delicate.

14. If any compound of manganese in a state of minute division is fused with 2 or 3 parts of *sodium carbonate* on a platinum wire, or on a small strip of platinum foil (heated by directing the flame against the lower surface), or upon the cover of a platinum crucible in the *outer* flame of the BUNSEN lamp, blowpipe, or blast-lamp, SODIUM MANGANATE, Na_2MnO_4, is formed, which makes the fused mass appear GREEN while hot, and of a BLUISH-GREEN tint after cooling, the mass at the same time losing its transparency. This reaction enables us to detect the smallest traces of manganese. It also succeeds very well with sodium peroxide (HEMPEL).

15. In the outer gas or blowpipe flame, *borax* and *sodium metaphosphate* dissolve manganese compounds to clear VIOLET-RED beads, which upon cooling acquire an AMETHYST-RED tint. They lose their color in the inner flame, owing to a reduction of manganic borate or phosphate to manganous salts. The borax bead appears black when containing a considerable portion of manganic borate, but that formed by sodium metaphosphate never loses its transparency. The latter bead, also, loses its color in the inner flame of the blowpipe far more readily than the former.

16. In relation to the microscopic detection of manganese, see HAUSHOFER, p. 96; BEHRENS, Zeitschr. f. analyt. Chem., **30**, 140.

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* The lead dioxide should first be tested to find whether it is free from manganese, by evaporating with sulphuric acid until most of the excess of this is removed, and boiling with dilute nitric acid and more of the lead dioxide.

§ 124.

c. NICKEL, Ni. (*Nickelous Oxide*, NiO.)

1. Metallic nickel, when it has been fused, is yellowish-white, inclining to gray. It is bright, hard, malleable, difficultly fusible, and does not oxidize in the air at the common temperature, but oxidizes slowly upon ignition. It is attracted by the magnet, and may itself become magnetic. Upon the application of heat, it slowly dissolves in hydrochloric and dilute sulphuric acids, with evolution of hydrogen gas, but it dissolves readily in nitric acid. The solutions contain nickelous salts.

2. NICKELOUS HYDROXIDE is light green, and remains unaltered in the air, but is converted by ignition at a white heat into amorphous, green NICKELOUS OXIDE (NiO). Both nickelous oxide and the corresponding hydroxide are readily soluble in hydrochloric, nitric, and sulphuric acids. The nickelous oxide which crystallizes in octahedrons is insoluble in acids, but dissolves in fusing potassium disulphate. NICKELIC OXIDE, Ni_2O_3, is black, and dissolves in hydrochloric acid to nickelous chloride, with evolution of chlorine. By gentle ignition of the nitrate, nickelous oxide of a grayish-green color, and containing a little nickelic oxide, is obtained.

3. Most of the NICKELOUS SALTS are yellow in the anhydrous, and green in the hydrated, state, their solutions being light green. They are decolorized by the addition of a certain amount of a cobaltous salt solution, 3Ni : 1Co. The soluble, normal salts slightly redden litmus-paper. Generally, the oxygen salts containing volatile acids are readily decomposed by ignition, but nickelous sulphate withstands a low red heat.

4. *Hydrogen sulphide* does not precipitate solutions of nickel salts with strong acids in presence of free acids. In the absence of the latter, a small portion of the nickel gradually separates as black, hydrous NICKEL SULPHIDE, NiS. Nickel acetate is not, or is scarcely at all, precipitated in presence of free acetic acid, but in the absence of the free acid, the greater part of the nickel is thrown down by long-continued action of hydrogen sulphide. If the solution, however, contains a suf-

ficient amount of alkali-metal acetate, the nickel is all precipitated, even in the presence of free acetic acid, especially by the action of hydrogen sulphide with the aid of heat. Free formic and monochloracetic acids also prevent the precipitation, but if their alkali-metal salts are present, the precipitation, upon heating, is only prevented by considerable amounts of the free acids.

5. *Ammonium sulphide* in neutral, and hydrogen sulphide in alkaline, solutions produce a black precipitate of hydrous NICKEL SULPHIDE, NiS, which is not altogether insoluble in ammonium sulphide, especially if the latter contains free ammonia. The fluid from which the precipitate has been thrown down usually exhibits, therefore, a brownish color, and upon neutralizing with acetic acid and warming, gives a slight precipitate of nickel sulphide. The presence of ammonium chloride, and especially of ammonium acetate, considerably promotes the precipitation. Ammonium sulphide which has been decolorized by sodium sulphite precipitates the nickel completely in the presence of ammonium salts and the absence of large amounts of free ammonia (LECRENIER). Nickel sulphide dissolves scarcely at all in acetic acid, with great difficulty in dilute hydrochloric acid, but readily in nitric and in nitro-hydrochloric acid upon application of heat.

6. *Potassium* and *sodium hydroxides* produce a light green precipitate of NICKELOUS HYDROXIDE, $Ni(OH)_2$, which is insoluble in an excess of the precipitants, and unalterable in the air and on boiling (even in the presence of hydrogen peroxide, iodine, or alcohol). Ammonium carbonate dissolves this precipitate, when filtered and washed, to a greenish-blue fluid, from which caustic potash or soda reprecipitates the nickel as apple-green hydroxide.

7. *Ammonia* added in small quantity produces a trifling greenish turbidity, but upon further addition of the reagent, this redissolves readily to a blue fluid containing a compound of NICKELOUS SALT AND AMMONIA. From this solution, potassium and sodium hydroxides precipitate nickelous hydroxide. Solutions containing ammonium salts or free acid are not rendered turbid by ammonia.

8. If the solution of a nickelous salt is treated with *potassium* or *sodium hydroxide*, and *bromine-water* or a solution of

sodium hypochlorite is added in sufficient quantity, but not hydrogen peroxide or iodine (difference from cobalt), and heat is applied, all the nickel separates as black NICKELIC HYDROXIDE, which dissolves immediately upon the addition of potassium cyanide, in the form of potassium nickelous cyanide. It is also reduced by a mixture of ammonia and ammonium chloride, going into solution as an ammonia-nickelous salt. The mixture just mentioned should be allowed to act upon the precipitate after the latter has been separated from the liquid. The solution takes place somewhat slowly in the cold, but quickly by heating.

N.B.—The presence of non-volatile, organic acids and also of sugar prevents or interferes with the precipitation of nickel as nickelous or nickelic hydroxide.

9. *Potassium ferrocyanide* precipitates from solutions of nickelous salts, greenish-white NICKEL FERROCYANIDE, $Ni_2Fe(CN)_6$, which is difficultly soluble in hydrochloric acid.

10. *Potassium ferricyanide* precipitates yellowish-brown NICKEL FERRICYANIDE, which is difficultly soluble in hydrochloric acid. In the presence of ammonium chloride or tartaric acid and an abundant excess of ammonia, a clear liquid is obtained, which is brownish-yellow or, if very dilute, pale yellow.

11. *Potassium cyanide* produces a greenish precipitate of NICKEL CYANIDE, $Ni(CN)_2$, which in an excess of the precipitant redissolves readily as a double nickel potassium cyanide, $Ni(CN)_2.2KCN$. The solution is brownish-yellow, and does not acquire a darker color on exposure to the air. If sulphuric or hydrochloric acid is added to this solution, the potassium cyanide is decomposed, and the nickel cyanide reprecipitated, although from highly dilute solutions, it separates only after some time. It is very difficultly soluble in an excess of the precipitating acids in the cold, but more readily so upon boiling. If the solution of the double cyanide is rendered alkaline by sodium hydroxide, being also kept in this condition by a further addition of the latter if necessary, and chlorine is passed into it without warming, or bromine is added, the *whole* of the nickel gradually separates as black nickelic hydroxide.

12. On adding a solution of *potassium thiocarbonate*,* to solutions which are not too dilute and which have been rendered alkaline by ammonia, a deep brownish-red fluid is obtained, which is barely translucent, and appears almost black by reflected light. If the solution of nickel is extremely dilute, the addition of the reagent will produce a yellowish-red color (C. D. BRAUN). The occurrence of this color in highly dilute solutions is characteristic of nickel. In the presence of cobalt, this reaction is almost or completely hidden, and it is more or less obscured in the presence of manganese and zinc.

13. On digestion in the cold, *barium carbonate* does not precipitate solutions of nickel salts, solution of sulphate alone excepted.

14. *Potassium nitrite* with acetic acid does not throw down nickel, even from concentrated solutions. In the presence of calcium, barium, or strontium, however, a yellow, crystalline nitrite of potassium, nickel, and the alkali-earth metal is precipitated from not too dilute solutions. The precipitate is difficultly soluble in cold water, but more readily so in hot water to a green fluid (KÜNZEL, O. L. ERDMANN).

15. In the outer flame, *borax* and *sodium metaphosphate* dissolve compounds of nickel to clear beads. The borax bead is violet while hot, and reddish-brown when cold. The sodium metaphosphate bead is reddish or brownish-red while hot, and yellow or reddish-yellow when cold. Small amounts of cobalt hide the colorations. In the inner flame, the sodium metaphosphate bead remains unaltered, but the borax bead becomes gray and cloudy from reduced metal. On continued heating, the particles of nickel collect together without fusing, and the bead loses its color.

16. By the reduction in the *stick of charcoal*, according to p. 34, the compounds of nickel yield, after trituration, white, shining, ductile spangles, which attach themselves to the point of a magnetic knife in the form of a brush. With nitric acid, they give a green solution, which can be further examined.

* To prepare potassium thiocarbonate, K_2CS_3, saturate one half of a solution of potassium hydroxide containing about 5 per cent of this substance with hydrogen sulphide, add the other half, and digest at a gentle heat with $\frac{1}{10}$ of its volume of carbon disulphide; separate the dark red liquid from the undissolved carbon disulphide and preserve it in well closed bottles.

17. In relation to the microscopic detection of nickel, see HAUSHOFER, p. 63; BEHRENS, Zeitschr. f. analyt. Chem., **30**, 141.

§ 125.

d. COBALT, Co. (*Cobaltous Oxide*, CoO.)

1. METALLIC COBALT which has been fused is steel-gray, rather hard, capable of taking a polish, malleable, difficultly fusible, and magnetic. It does not oxidize in the air at the common temperature, but it oxidizes at a red heat. With acids it behaves like nickel, and the solutions contain cobaltous salts.

2. COBALTOUS OXIDE, CoO, is light brown; cobaltous hydroxide is a pale red powder. Both dissolve readily in hydrochloric, nitric, and sulphuric acids. COBALTIC OXIDE, Co_2O_3, is black, and dissolves in hydrochloric acid to cobaltous chloride, with evolution of chlorine.

3. The COBALTOUS SALTS containing water of crystallization are red; the anhydrous salts are mostly blue. Moderately concentrated solutions appear of a light red color, which they retain when considerably diluted. The soluble normal salts redden litmus slightly; the salts containing volatile oxygen acids are generally readily decomposed at a red heat, although cobaltous sulphate can bear a moderate red heat without suffering decomposition. When a solution of cobaltous chloride is evaporated, the light red color changes to blue toward the end of the operation, but addition of water restores the red color.

4. *Hydrogen sulphide* does not give precipitates in solutions of salts with strong acids, if they contain free acid, but from neutral solutions, it gradually precipitates part of the cobalt as black, hydrous cobaltous sulphide, CoS. Cobaltous acetate does not give a precipitate, or gives only a very slight one, in presence of free acetic acid; but in the absence of free acid, the metal is almost or completely precipitated. If the solution, however, contains an alkali-metal acetate in sufficient amount, all the cobalt is thrown down, even in the presence of free acetic acid, especially by the action of hydrogen

sulphide with the aid of heat. Free formic and monochloracetic acids also prevent the precipitation; but if alkali-metal salts of these acids are present, the precipitation is prevented only by larger amounts of the acids.

5. *Ammonium sulphide* from neutral, and hydrogen sulphide from alkaline, solutions precipitate the whole of the metal as black, hydrous COBALTOUS SULPHIDE, CoS. Ammonium chloride promotes the precipitation most materially. Cobaltous sulphide is insoluble in alkalies and ammonium sulphide, scarcely soluble in acetic acid, very difficultly so in hydrochloric acid, and almost not at all if the cobalt sulphide has been precipitated at a boiling temperature. Nitric acid, as well as nitro-hydrochloric acid, dissolve cobalt sulphide upon heating.

6. *Potassium* and *sodium hydroxide* produce blue precipitates of BASIC COBALTOUS SALTS, which are insoluble in an excess of the precipitant when the dilution is sufficient. They become dirty green and afterwards grayish-yellow in the air, in consequence of the absorption of oxygen. Upon boiling, they are converted into pale red COBALTOUS HYDROXIDE, which contains alkali, and generally appears rather discolored from cobaltic hydroxide formed in the process. If, before boiling, alcohol is added, the precipitate is rapidly converted into dark brown cobaltic hydroxide. Ammonium chloride, if present in sufficient amount, prevents the precipitation by caustic alkalies. Normal ammonium carbonate completely dissolves the washed precipitates of cobaltous basic salts or cobaltous hydroxide to intense violet-red fluids, in which a somewhat large proportion of caustic potash or soda produces blue precipitates, the liquids still retaining their violet colors. However, if very *concentrated potassium hydroxide* solution is added in excess to the solution of a cobaltous salt, or if cobaltous hydroxide is heated with very little water and a piece of solid potassium hydroxide, the cobaltous hydroxide dissolves as such (DONATH) to a blue liquid.

7. *Ammonia* produces the same precipitate as potassium hydroxide, but this redissolves in an excess of the ammonia (leaving behind green flocks) to a brownish-yellow fluid, which turns brownish-red on exposure to the air, and from which caustic potash or soda throws down a portion of the cobalt

as blue basic salt. Ammonia produces no precipitate in solutions containing ammonium salts or a free acid.

8. If the solution of a cobaltous salt is treated with *potassium* or *sodium hydroxide*, and then *bromine-water*, a solution of *sodium hypochlorite*, *hydrogen peroxide*, or *iodine* is added, and the solution is boiled, all the cobalt separates (if the dilution is sufficient) as brownish-black COBALTIC HYDROXIDE. This is not soluble either in a mixture of ammonia and ammonium chloride or in potassium cyanide, but if nickelic hydroxide is present at the same time in large amount, potassium cyanide dissolves the cobaltic hydroxide with the nickelic hydroxide.

N.B.—The presence of non-volatile organic acids or of sugar interferes with or prevents the precipitation of cobalt as cobaltous or cobaltic hydroxide.

9. From cobaltous solutions, *potassium ferrocyanide* throws down green COBALTOUS FERROCYANIDE, $Co_2Fe(CN)_6$, which is difficultly soluble in hydrochloric acid.

10. *Potassium ferricyanide* throws down COBALTOUS FERRICYANIDE, which is hardly soluble at all in hydrochloric acid. If the cobaltous solution is first treated with tartaric acid or ammonium chloride, and then with ammonia in excess, so that a clear, strongly ammoniacal liquid is produced, and potassium ferricyanide is then added, a deep yellowish-red solution is obtained with rather concentrated cobalt solutions, the color of which can be recognized even at a great degree of dilution (SKEY, GINTL). The reaction is very delicate, and well adapted for detecting cobalt in presence of nickel.

11. Addition of *potassium cyanide* gives rise to the formation of a brownish-white precipitate of COBALTOUS CYANIDE, $Co(CN)_2$, which dissolves readily in excess of the precipitant as a double potassium cobaltous cyanide. Acids precipitate cobaltous cyanide from the solution, but if the latter is boiled with potassium cyanide in excess, in presence of free hydrocyanic acid (liberated by addition of a drop or two of hydrochloric acid), or if it is mixed with potassium or sodium hydroxide and chlorine is passed through it without warming, or bromine water is added, the double cyanide is converted into potassium cobalticyanide, $K_6Co_2(CN)_{12}$, and acids

will now produce no precipitate (essential difference from nickel). Potassium nitrite and acetic acid added to the unaltered solution of the double cyanide produce a blood-red color, in consequence of the formation of cobalt potassium nitrocyanide, but when the liquid is very dilute, the color is merely orange-red. Solution of sodium hydroxide added to the potassium cobaltous cyanide solution occasions a brown color when the fluid is shaken, oxygen being absorbed (C.D. BRAUN); while if it is treated with yellow ammonium sulphide, it assumes a blood-red color (TATTERSALL and PAPASOGLI). By the latter reaction, cobalt is essentially distinguished from nickel.

12. *Potassium thiocarbonate*, added to solutions which have been rendered alkaline by ammonia, produces a dark brown, almost black, color, but if the solution is extremely dilute, a wine-yellow color.

13. *Barium carbonate* behaves to cobaltous solutions in the same way as to solutions of nickelous salts.

14. If *potassium nitrite* is added in not too small proportion to the solution of a cobaltous salt, then acetic acid to *strongly* acid reaction, and the mixture put in a moderately warm place, all the cobalt separates (from concentrated solutions very soon and from dilute solutions after some time) in the form of a crystalline precipitate of a fine yellow color (FISCHER, STROMEYER). This is called FISCHER'S SALT, or, according to STROMEYER, POTASSIUM COBALTIC NITRITE. Various views prevail concerning its composition, the following being the most probable formula: $2K_3Co(NO_2)_6.3H_2O$. The precipitate is very perceptibly soluble in pure water, scarcely so in concentrated solutions of potassium salts and in alcohol, and insoluble in the presence of potassium nitrite. When boiled with water, it dissolves, though not copiously, to a red fluid, which remains clear upon cooling, and from which alkalies throw down cobaltous hydroxide. This is an excellent reaction, which serves well to distinguish and separate cobalt from nickel.

15. Upon adding an equal volume of hydrochloric acid of 20 per cent hydrogen chloride to a solution containing cobalt as sulphate or chloride, warming, and adding a hot solution of *nitroso-β-naphthol* in 50 per cent acetic acid, a voluminous,

purple-red precipitate of cobalti-nitroso-β-naphthol is formed (essential difference and means of separating cobalt from nickel, the salts of the latter not being precipitated in the presence of a sufficient amount of hydrochloric acid). Care should be taken not to confuse with cobalti-nitroso-β-naphthol a slight separation of nitroso-β-naphthol, which may take place upon adding an abundant amount of its acetic acid solution to hot water containing hydrochloric acid. Cobalti-nitroso-β-naphthol, $(C_{10}H_6ONO)_3Co$, is stable in the highest degree towards acids, alkalies, and oxidizing and reducing agents. By warming it with ammonium sulphide, however, cobalt sulphide is formed (ILINSKI and VON KNORRE).

16. In the inner and outer flames, *borax* dissolves compounds of cobalt to clear beads of a magnificent blue color, which appear violet by candle-light, and are almost black in the presence of a large quantity of cobalt. This test is as delicate as it is characteristic. *Sodium metaphosphate* gives the same reaction, but it is less delicate.

17. In the reduction with the *stick of charcoal*, according to p. 35, compounds of cobalt behave in the same way as compounds of nickel. The solution with nitric acid is red.

18. Concerning the microscopic detection of cobalt, see HAUSHOFER, p. 63; BEHRENS, Zeitschr. f. analyt. Chem., **30**, 140.

§ 126.

e. IRON, Fe, IN FERROUS COMPOUNDS. (*Ferrous Oxide*, FeO.)

1. METALLIC IRON in the pure state has a light whitish-gray color (iron containing carbon is more or less gray). The metal is hard, lustrous, malleable, ductile, exceedingly difficult to fuse, and is attracted by the magnet. In contact with air and moisture, a coating of rust (ferric hydroxide) forms on its surface, and upon ignition in the air, a coating of black ferrous-ferric oxide, Fe_3O_4, is produced. Hydrochloric and dilute sulphuric acids dissolve iron, with evolution of hydrogen; if the iron contains carbide, the hydrogen is mixed with hydrocarbons. The solutions contain ferrous salts. Dilute nitric acid dissolves iron (according to its relative quantity, the degree of dilution, and the temperature) either without

the evolution of gas, but with the formation of ammonium nitrate, to ferrous nitrate, or with the evolution of nitrous or nitric oxide, to ferric nitrate. If the iron contains carbide, some carbon dioxide is also evolved, and there is left undissolved a brown substance resembling humus, which is soluble in alkalies; when graphite is present, it, also, is left behind.

2. FERROUS OXIDE is black; ferrous hydroxide is white, and in the moist state absorbs oxygen and speedily acquires a grayish-green and ultimately a brownish-red color. Both ferrous oxide and ferrous hydroxide are readily dissolved by hydrochloric, sulphuric, and nitric acids.

3. In the anhydrous state, the FERROUS SALTS have a white, in the hydrated state a greenish, color, but their solutions look greenish only when concentrated. The solutions absorb oxygen when exposed to the air, and are converted more or less completely into ferric salts, with precipitation of basic ferric salts. Chlorine, bromine, hydrogen peroxide, or nitric acid, upon boiling, convert them quickly and completely into ferric salt solutions. In relation to the brownish-black coloration of the solution, which appears transiently during the oxidation by nitric acid, compare nitric acid, Section III. The soluble, normal ferrous salts do not redden litmus-paper, but this is the case only when they are entirely pure and free from ferric salts. Ferrous salts which contain volatile oxygen acids are decomposed by ignition.

4. Solutions of ferrous salts made acid by strong acids are not precipitated by *hydrogen sulphide;* nor are neutral solutions or solutions acidified with weak acids precipitated by this reagent, or at the most but very incompletely. Solutions containing sodium acetate and some free acetic acid are only very incompletely precipitated, even upon heating. Monochloracetic or formic acid, added in sufficient amount, prevents the precipitation, even when alkali-metal salts of these acids are present.

5. *Ammonium sulphide* from neutral, and hydrogen sulphide from alkaline, solutions, precipitates the whole of the metal as black, hydrous FERROUS SULPHIDE, FeS, which is insoluble in the hydroxides and sulphides of the alkali-metals, but dissolves readily in hydrochloric and nitric acids. This black precipitate turns reddish-brown in the air by oxidation. To

highly dilute solutions, ammonium sulphide imparts a green color, and it is only after some time that the ferrous sulphide separates as a black precipitate. Ammonium chloride promotes the precipitation most materially.

6. *Potassium hydroxide, sodium hydroxide,* and *ammonia* produce a precipitate of FERROUS HYDROXIDE, $Fe(OH)_2$, which at the first moment looks almost white, but acquires after a very short time a dirty green and ultimately a reddish-brown color, owing to absorption of oxygen from the air. Presence of ammonium salts partly prevents the precipitation by potassium hydroxide, and wholly prevents that by ammonia. If alkaline ferrous solutions thus obtained by the agency of ammonium salts are exposed to the air, ferrous-ferric and ferric hydroxides precipitate. Non-volatile organic acids, sugar, etc., check or prevent the precipitation by alkalies.

7. *Potassium ferrocyanide* produces a bluish-white precipitate of POTASSIUM FERROUS FERROCYANIDE, $K_2Fe_2(FeC_6N_6)_2$, which by absorption of oxygen from the air speedily acquires a blue color. Nitric acid or chlorine converts it immediately into Prussian blue: $3K_2Fe_2(FeC_6N_6)_2 + 9Cl = 6KCl + FeCl_3 + 2Fe_4(FeC_6N_6)_3$. The precipitate also forms in an ammoniacal solution containing ammonium tartrate.

8. *Potassium ferricyanide* produces a magnificent, blue precipitate of FERROUS FERRICYANIDE (TURNBULL'S blue), $Fe_3(FeC_6N_6)_2$. This does not differ in color from Prussian blue. It is insoluble in hydrochloric acid, but is readily decomposed by potassium hydroxide. In highly dilute solutions, the reagent produces simply a deep blue-green coloration.

9. *Potassium sulphocyanide* does not alter solutions of ferrous salts when free from ferric salts.

10. In the cold, *barium carbonate* does not precipitate solutions of ferrous salts, with the exception of the sulphate.

11. *Borax* dissolves ferrous compounds in the oxidizing flame, giving beads varying in color from yellow to a dark red; when cold, the beads vary from colorless to dark yellow. In the inner flame, the beads change to bottle-green, owing to the reduction of the previously formed ferric borate to ferrous-ferric borate. *Sodium metaphosphate* shows a similar reaction. Upon cooling, the beads produced with this reagent lose their color still more completely than those pro-

duced with borax, and the signs of the ensuing reduction in the reducing flame are also less marked.

12. When reduced in the *stick of charcoal* (p. 34), ferrous compounds give a dull black powder, which is attracted by a magnet. When dissolved in a few drops of aqua regia, the reduced metal gives a yellow fluid, which can be further tested according to § 127.

13. Concerning the microscopic detection of ferrous iron, compare HAUSHOFER, p. 49.

§ 127.

f. IRON, Fe, IN FERRIC COMPOUNDS. (*Ferric Oxide*, Fe_2O_3.)

1. Native, crystallized FERRIC OXIDE, Fe_2O_3, is steel-gray. Upon trituration, the native as well as the artificially prepared ferric oxide gives a brownish-red powder. The color of the ferric hydroxides is more inclined to reddish-brown. Ferric hydroxide dissolves in hydrochloric, nitric, and sulphuric acids. The oxide is more difficultly soluble, but dissolves upon long digestion with the aid of heat, especially in hydrochloric acid, and by fusion with potassium disulphate. FERROUS-FERRIC OXIDE, Fe_3O_4, is black, and dissolves in hydrochloric acid to ferrous and ferric chlorides, and in aqua regia to ferric chloride.

2. The normal, anhydrous FERRIC SALTS are nearly white, but the basic salts are yellow or reddish-brown. The color of the solutions is brownish-yellow, and becomes reddish-yellow upon the application of heat. The soluble, normal salts redden litmus-paper. The ferric salts of volatile oxygen acids are decomposed by ignition.

3. In solutions made acid by stronger acids, *hydrogen sulphide* produces a milky-white turbidity, proceeding from separated SULPHUR, the ferric salt being at the same time converted into ferrous salt: $Fe_2(SO_4)_3 + H_2S = 2FeSO_4 + H_2SO_4 + S$.

If a solution of hydrogen sulphide is rapidly added to neutral solutions, a transient bluing of the fluid also occurs. From solution of normal ferric acetate, hydrogen sulphide

throws down the greater part of the iron; but in presence of a sufficient quantity of free acetic acid, sulphur alone separates. Upon treatment with hydrogen sulphide in the cold, a solution of a ferric salt containing sodium acetate and much free acetic acid gives scarcely anything but a separation of sulphur, but when warm, a part of the iron may precipitate as ferrous sulphide. Monochloracetic acid and formic acid, when present in sufficient amount, prevent the precipitation, even when the alkali-metal salts of these acids are present, and when the liquids are heated.

4. *Ammonium sulphide* from neutral, and hydrogen sulphide from alkaline, solutions precipitate the whole of the metal as black FERROUS SULPHIDE, FeS, mixed with sulphur: $2FeCl_3 + 3(NH_4)_2S = 6NH_4Cl + 2FeS + S$. In very dilute solutions, the reagent produces only a blackish-green coloration, and in such cases, the minutely divided ferrous sulphide subsides only after long standing. Ammonium chloride most materially promotes the precipitation. The properties of ferrous sulphide have been given under ferrous compounds.

5. *Potassium hydroxide*, *sodium hydroxide*, and *ammonia* produce bulky, reddish-brown precipitates of FERRIC HYDROXIDE, $Fe(OH)_3$, which are insoluble in an excess of the precipitant as well as in ammonium salts. Non-volatile organic acids or sugar, when present in sufficient quantity, entirely prevent the precipitation.

6. Even in highly dilute solutions, *potassium ferrocyanide* produces a magnificent blue precipitate of FERRIC FERROCYANIDE (Prussian blue), $Fe_4(FeC_6N_6)_3$: $4FeCl_3 + 3K_4Fe(CN)_6 = 12KCl + Fe_4(FeC_6N_6)_3$. This is insoluble in hydrochloric acid, but is decomposed by potassium hydroxide, with separation of ferric hydroxide. Prussian blue is somewhat soluble in an excess of potassium ferrocyanide. In solutions containing very much hydrochloric acid, or in neutral solutions containing very much ammonium chloride, small amounts of ferric compounds cannot be detected by means of potassium ferrocyanide. In the solutions containing ammonium chloride, the reaction makes its appearance only upon the addition of some hydrochloric acid (VULPIUS). Solutions of ferric salts which have been made ammoniacal after the addition

of tartaric acid are not precipitated by potassium ferrocyanide (difference from manganese, L. BLUM).

7. *Potassium ferricyanide* deepens the color of solutions of ferric salts to reddish-brown, but it fails to produce a precipitate.

8. *Potassium sulphocyanide*, if not added in too small a quantity, imparts to *acid* solutions a most intense, blood-red color, arising from the formation of a soluble POTASSIUM FERRIC SULPHOCYANIDE (KRÜSS and MORAHT). This color does not disappear on the addition of a little alcohol and warming (difference from the analogous reaction of nitrous acid, § 189). Solutions of ferric salts containing sodium acetate (which consequently are more or less red from ferric acetate) do not show the blood-red color of the sulphocyanide till after the addition of much hydrochloric acid. The same is the case when the solution contains oxalic, tartaric, citric, malic, iodic, phosphoric, arsenic, and hydrofluoric acids. In the presence of nitric acid, the reaction must be carried out in the cold. This test will indicate the presence of iron, even in fluids which are so highly dilute that every other reagent fails to produce in them the slightest visible alteration. In such cases, the red coloration may be detected most distinctly by resting the test-tube upon a sheet of white paper, and looking through it from the top. The delicacy of the reaction may be also increased by shaking gently with ether, after the addition of hydrochloric acid and of excess of potassium sulphocyanide solution freshly prepared from the crystals. The ferric sulphocyanide dissolves in the ether, and the layer of the latter acquires a more or less red color.

9. If a small amount of the solution of a ferric compound is added to the blue liquid obtained by adding a little *cobalt chloride* or *nitrate* to *fuming hydrochloric acid*, the blue color changes to GREEN. The reaction is especially adapted for recognizing ferric compounds in acids or in the presence of ferrous salts (VENABLE).

10. Even in the cold, *barium carbonate* precipitates all the iron as FERRIC HYDROXIDE MIXED WITH A BASIC SALT.

11. The reactions before the *blowpipe* are the same as with the ferrous compounds.

12. In reference to the microscopic detection of ferric

compounds, see HAUSHOFER, p. 48; BEHRENS, Zeitschr. f. analyt. Chem., **30**, 160.

§ 128.

Recapitulation and Remarks.—In carrying out analyses, the members of Group IV are generally obtained as hydrated sulphides by precipitating their solution with ammonium sulphide. We shall first consider the methods by which the metals contained in such a precipitate can generally be best separated from each other and detected when all are present, on the basis of the reactions which have been described in the preceding paragraphs, and then we shall mention some further methods, which offer special advantages in certain cases.

1. Since cobalt and nickel sulphides are but slightly soluble in dilute hydrochloric acid, especially if it contains hydrogen sulphide, while ferrous sulphide and manganese and zinc sulphides are readily soluble in it, it is generally most convenient to separate cobalt and nickel, or at least by far the greater portion of them, upon this basis. For this purpose, the moist precipitate of the sulphides is treated with a mixture of 5 parts of hydrogen sulphide water and 1 part of ordinary hydrochloric acid of 1.12 sp. gr.,* with active stirring, but without warming. Nickel and cobalt sulphides then remain almost completely undissolved, while the other sulphides dissolve as chlorides, with the evolution of hydrogen sulphide. The precipitate is filtered off and washed with water, to which it is best to add a little hydrogen sulphide water.

We shall next consider the precipitate which remained undissolved and afterwards the liquid which was filtered from it.

2. Since cobalt can be separated from nickel only by having both in solution, it is first necessary to dissolve the precipitate. It is therefore best to dry the filter containing

* If the precipitate contains a considerable amount of other sulphides, the hydrochloric acid may be diluted with water instead of hydrogen sulphide water, in this case, because a sufficient amount of hydrogen sulphide is evolved during the treatment.

the precipitate, then ignite it with access of air in a porcelain crucible, until the carbon of the filter has been consumed, and warm the residue with hydrochloric acid with the addition of a few drops of nitric acid. If much iron was present, this solution usually contains a small amount of this metal, together with the cobalt and nickel. After the addition of water, therefore, it is treated with ammonia in moderate excess, and filtered if necessary. The ammoniacal solution is evaporated to dryness in a small porcelain dish, the ammonium salts are driven off by gentle ignition, the residue is dissolved in hydrochloric acid with a few drops of nitric acid, the solution is evaporated to a small volume, sodium carbonate is carefully added to alkaline, then acetic acid to strongly acid, reaction, and finally potassium nitrite (§ 125, 14). By allowing the liquid to stand at a gentle heat, the cobalt separates quickly if it is present in considerable amount, or after a longer time if only a little is present, in the form of yellow potassium cobaltic nitrite. A filtration is made after about 12 hours, and the nickel in the filtrate is precipitated with potassium or sodium hydroxide. For the sake of certainty, both precipitates should be tested in the borax bead (§ 125, 16, and § 124, 15). The separation of cobalt from nickel by means of nitroso-β-naphthol more readily gives occasion for mistakes.

3. The solution filtered from the precipitate of cobalt and nickel sulphides contains the iron as ferrous chloride, also manganous and zinc chlorides, as well as small amounts of cobalt and nickel chlorides. Since iron can be easily separated from the other metals only when it is present as a ferric compound, the liquid is first boiled in order to drive off the hydrogen sulphide, and nitric acid is added to the gently boiling solution until the ferrous chloride is completely converted into ferric chloride. In case of doubt, the testing of a few drops with potassium ferricyanide leads to certainty. The solution is now allowed to cool, and the iron is separated as a basic ferric salt. For accomplishing this end, one of the following methods may be chosen:

a. The free acid is almost neutralized by the careful addition of sodium carbonate; barium carbonate, suspended in water, is then added until a small portion of it remains undis-

solved; it is well stirred, allowed to settle, and filtered. *b.* The solution is diluted sufficiently, a rather large quantity of ammonium chloride is added, then ammonium carbonate carefully, using at last a dilute solution of it, until the liquid, while still showing an acid reaction, begins to be turbid. The liquid is then heated to boiling for a short time, allowed to settle somewhat, and filtered hot. *c.* The solution is diluted, sodium carbonate is added until the acid is almost neutralized, sodium acetate is added to the solution, which should be clear and have a distinct acid reaction; it is then heated to boiling, allowed to settle a little, and filtered hot.

Whichever of these methods is used, the ochre-like color of the precipitate generally allows the presence of iron to be recognized conclusively. In case of doubt, a portion of the precipitate may be dissolved in hydrochloric acid, and the diluted solution tested with potassium ferrocyanide or sulphocyanide.

4. The liquid filtered from the basic ferric salt now contains manganous chloride, zinc chloride, and small amounts of cobalt and nickel chlorides. For the separation of manganese from the other metals, the solubility of manganous sulphide in acetic acid offers a good means. Upon this basis, the separation may be made according to one of the following methods:

a. To the solution contained in a small flask, after the addition of ammonium chloride, ammonia is added to alkaline reaction, then ammonium sulphide; it is allowed to stand at a gentle heat, filtered, the precipitate is washed with water, to which a little hydrogen sulphide water is added; the filter containing the precipitate is then spread out in a small porcelain dish; a mixture of about equal parts of acetic acid of 1.04 sp. gr. and water is poured over it; this is allowed to act about five minutes, when it is diluted with water, filtered, and the precipitate is washed. *b.* (This is a more exact, but somewhat more complicated method.) If barium carbonate has been used for separating the iron, it is best, in the first place, to remove the barium from the solution by means of sulphuric acid. Ammonia is added in excess to the solution, then acetic acid to acid reaction; sodium acetate is next added, and hydrogen sulphide is passed into the solu-

tion while hot; it is now allowed to settle, filtered, and the precipitate washed.

In either case, the manganese, in the form of manganous acetate, is now in a solution which contains some free acetic acid and hydrogen sulphide, and may be separated from it, α, by adding ammonia and ammonium sulphide, so as to precipitate the manganese as sulphide; β, by evaporating the solution and precipitating the manganese as manganous or mangano-manganic hydroxide by the addition of potassium hydroxide; γ, by adding some bromine in hydrochloric acid to the solution until it is colored strongly yellow, then precipitating the manganese as hydrated dioxide by adding an excess of ammonia and boiling. Of these methods, the latter possesses greater delicacy, as well as the additional advantage that the brownish-black color of the precipitate generally makes further testing unnecessary. For confirmation, a small portion of the precipitated manganese compound may be fused with sodium carbonate according to § 123, 14.

5. The precipitate left undissolved by treating with acetic acid according to 4, *a*, or produced by hydrogen sulphide from the solution acidified with acetic acid according to 4, *b*, contains zinc sulphide, the white color of which is more or less concealed by the small quantities of cobalt and nickel sulphides which are mixed with it. In order to detect the zinc, the filter containing the precipitate is spread out in a porcelain dish, and a mixture of about 5 parts of hydrogen sulphide water and 1 part of ordinary hydrochloric acid of 1.12 sp. gr. is poured over it, allowed to act for a few minutes, and then the liquid containing the zinc as chloride is filtered from the nickel and cobalt sulphides remaining undissolved. If an excess of sodium acetate is now added to the filtrate, sodium chloride and acetic acid are formed by its action upon the hydrochloric acid; and since the liquid already contains hydrogen sulphide, the zinc separates as white zinc sulphide. The latter is free from the minute traces of nickel and cobalt which had gone into solution in hydrochloric acid, because their sulphides are not precipitated in the cold, under the prevailing conditions. If so little cobalt and nickel had been present that they were not found in 2, the sulphides remain-

ing behind in 5 should be tested for these metals according to the method given in 2.

We now pass on to other methods which offer advantages in certain cases. If it is desired to separate small amounts of iron in the ferric condition from the other metals of the fourth group, the end is readily reached by adding ammonium chloride and ammonia in moderate excess in the cold, and quickly filtering off the small amount of ferric hydroxide which separates. By delaying the filtration, a part of the manganese would separate with the iron as manganic hydroxide, in consequence of the action of the oxygen of the air. If this precitate is dissolved again in hydrochloric acid, the solution heated to boiling for some time, and then another precipitation made in the *cold* with an excess of ammonia, the separation of iron from the other metals is almost complete. In the presence of more considerable quantities of iron, the method is not to be recommended, because certain amounts of other hydroxides always precipitate with the ferric hydroxide, so that by the use of this process small quantities of other metals may be entirely overlooked.

If it is desired to separate zinc from the other metals of the fourth group, one of the following methods may also be used: *a*. The solution is sufficiently diluted, the greater part of any free acid that may be present is neutralized with ammonia, ammonium monochloracetate and a little free monochloracetic acid are added, and a precipitation of zinc with hydrogen sulphide is made at a temperature of from 50° to 60°. The other metals remain in solution. *b*. Sodium carbonate is added to the solution until a permanent precipitate just begins to form, this is redissolved in a few drops of dilute hydrochloric acid, sodium thiosulphate is added in not too small amount, the solution is largely diluted, and hydrogen sulphide is passed in in the cold. Zinc precipitates as zinc sulphide, while the other metals remain in solution (J. RIBAN). *c*. If large amounts of zinc are to be separated from small amounts of the other metals, the solution may also be treated with potassium or sodium hydroxide. If an excess of this is added, the precipitated zinc hydroxide redissolves, while the hydroxides of the other metals remain behind. Zinc can be precipitated from the solution with ammonium sulphide.

This method seldom offers special advantages, because not inconsiderable quantities of zinc remain behind in the undissolved precipitate. The process would be entirely inadmissible if chromic hydroxide were present at the same time, since solutions of the latter and of zinc hydroxide in potassium or sodium hydroxide mutually precipitate each other.

Since a brown coloration of the liquid (which may occur in the presence of nickel when the precipitate obtained by the addition of ammonium chloride, ammonia, and ammonium sulphide to the solution of the metals of the fourth group is filtered) is a sufficient indication of the presence of nickel; and since it is often possible to recognize cobalt with certainty in the presence of nickel, by testing a little of the residue obtained after removing the ammonium salts according to 2, by means of the borax bead in the reducing flame, the separation of cobalt from nickel given above in 2, which requires considerable time, may sometimes be omitted. If it is desired to recognize small amounts of nickel in presence of large quantities of cobalt, the use of the solution of the cyanides of the metals in potassium cyanide, to which sodium hydroxide is added, is to be recommended. The red coloration produced in a portion of this liquid by the addition of yellow ammonium sulphide shows the presence of cobalt, while the separation of black nickelic hydroxide obtained by treatment with chlorine or bromine allows the nickel to be detected (§ 125, 11, and § 124, 11). The varying behavior of nickelic and cobaltic hydroxides to potassium cyanide solution, and also to ammonium chloride and ammonia (§ 124, 8, and 125, 8), is more appropriate for distinguishing than for separating nickel and cobalt.*

In the presence of non-volatile organic substances, the method depending upon the preliminary precipitation of all the metals as sulphides *must* be used for the separation of the members of the fourth group, because such organic substances would hinder or prevent the precipitation of iron as hydroxide or as a basic salt. In the presence of citric acid, even this

* Concerning the detection of nickel beside cobalt, see also HERRENSCHMIDT and CAPELLE, Zeitschr. f. analyt. Chem., 32, 608.

method does not suffice, because alkali-metal citrates prevent the precipitation of manganese as manganous sulphide; and therefore the solution should, in the first place, be evaporated with sodium carbonate, and ignited with the addition of potassium nitrate, in order to destroy the organic substances.

Ferrous and ferric salts may be detected in presence of each other by testing for the former with potassium ferricyanide, and for the latter with potassium ferrocyanide or sulphocyanide.

Special Reactions of the Rarer Metals of the Fourth Group.

§ 129.

1. Uranium, U.

This metal is found only sparingly, in pitchblende, uranium-ochre, etc. Its oxides are used for the production of a yellowish-green glass. Uranium forms three oxides, viz., uranous oxide, UO_2, uranic oxide, UO_3 (also called uranic acid), and peruranic acid, UO_4; the latter, however, is not known in the free state. Uranous oxide is brown or black, and dissolves in nitric acid to uranic nitrate. Uranic oxide is brick-red; uranic hydroxide, $UO_2(OH)_2$, is yellow. Both are converted by ignition into the dark blackish-green urano-uranic oxide, U_3O_8. The uranic salts are yellow. Most of them dissolve in water, and those which are insoluble in that liquid, almost without exception dissolve in hydrochloric acid. The solutions are yellow. If uranic salts in sulphuric acid solution are warmed with zinc, the color of the solution changes into the green color of uranous salts. *Hydrogen sulphide* does not alter solutions of uranic salts; but after neutralization of the free acid, *ammonium sulphide* throws down from them a slowly subsiding precipitate, which is readily soluble in acids, even acetic acid. The precipitation is promoted by ammonium chloride. The precipitate, when formed in the cold, is chocolate-brown, and contains uranic oxysulphide, ammonium sulphide, and water. It is insoluble in pure ammonium sulphide; but in that which is colorless and contains some ammonium carbonate, or in yellow ammonium sulphide, it dissolves to a brown liquid (Cl. Zimmermann). On being washed, the precipitate is gradually converted into yellow uranic hydroxide. On boiling the mixture of uranium solution and ammonium sulphide, the oxysulphide at first thrown down decomposes into sulphur and black uranous oxide, the latter being insoluble in the excess of ammonium sulphide (Remelé). The uranic oxysulphide (but not the precipitate which has been converted into uranous oxide and sulphur) dissolves readily in ammonium

carbonate (essential difference, and means of separating uranium from zinc, manganese, iron, etc.). If the oxysulphide remains long in contact with an excess of ammonium sulphide, it is converted, when air has access to it, into a red modification in consequence of the formation of ammonium thiosulphate; but when air is excluded, a black modification is formed. *Ammonia* and *potassium* and *sodium hydroxides* produce yellow precipitates containing uranic oxide and alkali, which are insoluble in excess of the precipitants, *e.g.*, $K_2U_2O_7$. Tartaric acid prevents or interferes with the precipitation, and ammonium chloride facilitates the precipitation by ammonia. *Ammonium carbonate* and *potassium* or *sodium bicarbonate* produce yellow precipitates of ammonium, sodium, or potassium uranic carbonate, *e.g.*, $2K_2CO_3.UO_2CO_3$, which *readily redissolve in an excess of the precipitants.* Potassium and sodium hydroxides throw down from such solutions the whole of the uranium. *Hydrogen peroxide* produces a yellowish-white precipitate, soluble in hydrochloric acid, which may be regarded as the hydroxide of a compound of one molecule of peruranic acid with two molecules of uranic oxide, or as uranium tetroxide, UO_4 (FAIRLEY). Ammonium carbonate dissolves this to an intensely yellow liquid. The reaction is very delicate. From acetic acid solutions, or from solutions to which sodium acetate is added, *sodium phosphate* precipitates yellowish-white uranyl phosphate, $HUO_2PO_4.xH_2O$, which is soluble in the mineral acids. In the presence of much ammonium salts, similarly colored ammonium uranyl phosphate, $NH_4UO_2PO_4.xH_2O$, is formed. Heating facilitates the separation of both precipitates. Solutions of uranic salts (that of the nitrate to a marked degree) color *turmeric-paper* brown, even in the presence of a little free hydrochloric acid, but in that case with less delicacy. Larger amounts of free mineral acids prevent the reaction (CL. ZIMMERMANN). When the turmeric-paper which is colored brown by uranium solution is dotted with a solution of sodium carbonate, *more deeply colored* brown spots are formed. *Barium carbonate* completely precipitates solutions of uranic salts, even in the cold (essential difference from nickel, cobalt, manganese, and zinc, and means of separating uranium from these metals).

Mercuric oxide, made into a slime with water, precipitates uranic solutions completely when they are boiled with it in the presence of ammonium chloride (means of separating uranium from strontium, calcium, and the alkali-metals, but not as good for barium, ALIBEGOFF). *Potassium ferrocyanide* produces a reddish-brown precipitate, or at least a coloration (a most delicate test). The precipitate dissolves in ammonium carbonate, giving a pale-yellow color. Upon heating, it is also soluble in dilute hydrochloric acid. With uranium compounds, in the inner flame of the blowpipe, *borax* and *sodium metaphosphate* give green beads; in the outer flame, yellow beads, which acquire a yellowish-green tint on cooling.

Concerning the microscopic detection of uranium, see HAUSHOFER, p. 132; BEHRENS, Zeitschr. f. analyt. Chem., 30, 169.

§ 130.

2. Thallium, Tl.

Thallium occurs in minute quantities, in many kinds of copper, in iron pyrites, and crude sulphur, and accumulates in the flue-dust of the lead chambers where the furnaces are fed with thalliferous pyrites. It is occasionally found in commercial sulphuric and hydrochloric acids, and has been discovered in lepidolite, preparations of cadmium and bismuth, in ores of zinc, mercury, and antimony, in the ashes of plants, and in some saline waters. Thallium is a metal resembling lead, of 11.8 to 11.9 sp. gr., soft, fuses at 285° to 290°, volatile at a white heat, crackling like tin when bent, and does not decompose water, except upon addition of acid. Dilute sulphuric and nitric acids readily dissolve it, but hydrochloric acid dissolves it with difficulty. It forms two oxides; thallious oxide, Tl_2O, and thallic oxide, Tl_2O_3. Thallious oxide is black, fusible, and when in the melted state, it attacks glass or porcelain. It dissolves in water to hydroxide, and the solution is colorless, alkaline, caustic, and absorbs carbonic acid. It also dissolves in alcohol. Thallic oxide is dark violet, and insoluble in water; thallic hydroxide is brown. Thallic oxide is scarcely acted on by concentrated sulphuric acid in the cold; but on heating, they combine. On continued heating, oxygen escapes, and thallious sulphate is formed. Treated with hydrochloric acid, thallic oxide yields the corresponding chloride, which may be obtained in the form of colorless, easily soluble crystals. When this is heated, chlorine escapes, while compounds of thallious and thallic chlorides result. Thallic salts are decomposed by water, with the separation of thallic hydroxide. In acid solutions of thallic salts, alkalies throw down thallic hydroxide. Hydrogen sulphide produces thallious salts, with separation of sulphur, potassium iodide yields thallious iodide and iodine, while hydrochloric acid produces no precipitate. The thallious salts are colorless; some are readily soluble in water (sulphate, nitrate, neutral phosphate, tartrate, acetate), others difficultly soluble (carbonate, tri-basic phosphate, chloride), while a few are almost insoluble (iodide, etc.). On boiling solutions of thallious salts with nitric acid, they are *not* converted into thallic salts, but they are so converted entirely by boiling with aqua regia. *Potassium hydroxide*, *sodium hydroxide*, and *ammonia* do not precipitate aqueous solutions of thallious salts. *Alkaline carbonates* throw down thallious carbonate, but only from very concentrated solutions (for 100 parts of water dissolve 5.23 parts at 18°). If the solutions are not extremely dilute, *hydrochloric acid* throws down thallious chloride in the form of a white, readily subsiding precipitate, unalterable when exposed to light, and still less soluble in dilute hydrochloric acid than in water. Even from the most dilute solutions, *potassium iodide* precipitates light yellow thallious iodide, which is almost insoluble in water (1 : 17000), and far less soluble in an excess of potassium iodide. In the cold, it dissolves difficultly in sodium thiosulphate solution

(difference from lead iodide, E. A. WERNER). From solutions which are not extremely dilute' *hydrochloroplatinic acid* precipitates pale orange thallious platinic chloride, Tl_2PtCl_6, which is very difficultly soluble. *Hydrogen sulphide* does not precipitate solutions rendered strongly acid by mineral acids (unless arsenious acid or antimonious oxide are present, in which case compounds of thallium sulphide with sulphides of arsenic or antimony separate as more or less orange-colored precipitates). Neutral or very slightly acid solutions are incompletely precipitated by this reagent, and from acetic acid solutions, the whole of the thallium is thrown down as black thallious sulphide. Colorless *ammonium sulphide* precipitates the whole of the thallium as black sulphide, which readily collects into lumps, especially on warming; and hydrogen sulphide added to alkaline solutions has the same effect. The sulphide thrown down is insoluble in ammonia, alkali-metal sulphides, and potassium cyanide, rapidly oxidizes in the air to thallious sulphate, dissolves readily in dilute hydrochloric, sulphuric, and nitric acids, but is acted on only with difficulty by acetic acid. On heating, it first fuses and then volatilizes. *Zinc* throws down the metal in the form of black, crystalline laminæ. *Colorless flames* are tinged intensely green by compounds of thallium. The *spectrum* of thallium exhibits only one line (compare the spectrum plate) of a magnificent, extremely characteristic, emerald-green color. If the quantity of metal is small, the line soon disappears. The spectroscope generally affords the best means of detecting thallium. Thalliferous pyrites often give the green line at once. To look for thallium in crude sulphur, it is best to remove the greater part of the sulphur with carbon disulphide, and then to test the residue. In the presence of much sodium with very small quantities of thallium, the green line will not be seen, unless the substance is moistened, and the spectrum examined which is first produced. If a precipitate obtained by hydrochloroplatinic acid is to be tested for traces of thallium platinic chloride in the presence of much potassium, rubidium, and cæsium platinic chlorides, it is boiled repeatedly with small quantities of water, and the residue remaining at last is tested spectroscopically for thallium. For the detection of thallium in the wet way, potassium iodide is the most delicate reagent; if a ferric salt is present, it should be previously reduced by sodium sulphite. Concerning the microscopic detection of thallium, see HAUSHOFER, p. 125, and BEHRENS, Zeitschr. f. analyt. Chem., 30, 138.

§ 131.

3. INDIUM, In. (*Oxide*, In_2O_3.)

Indium has hitherto been discovered only in the blende of Freiburg, in the zinc prepared from the same, and in wolfram. It is a white, highly lustrous metal, and resembles platinum in color. It is very soft, ductile, makes a mark on paper, is capable of receiving a polish, and is oxidized slowly

upon contact with air and water—less easily than zinc. Indium melts at 176°. On charcoal before the blowpipe, it melts with a shining metallic surface, colors the flame blue, and yields an incrustation, which is dark yellow while hot, light yellow when cold, and cannot be easily dispersed by the blowpipe flame. Indium dissolves in dilute hydrochloric and sulphuric acids, with evolution of hydrogen, slowly in the cold, but more rapidly on heating. In contact with cold, concentrated sulphuric acid, it also gives off hydrogen, while anhydrous indium sulphate separates. In nitric acid, it dissolves with ease even when the acid is cold and dilute. Indium oxide, In_2O_3, is reddish-brown when hot, very light yellow when cold, and does not color vitreous fluxes. When ignited in hydrogen or with charcoal, it is readily reduced, and if a flux is used, metallic globules are obtained. The ignited oxide dissolves slowly in acids in the cold, but readily and completely by the aid of heat. The salts are colorless, and the sulphate, nitrate, and the volatile, hygroscopic chloride dissolve readily in water. *Alkalies* throw down the hydroxide in the form of a white, bulky precipitate resembling aluminium hydroxide, but tartaric acid prevents the precipitation. Potassium or sodium hydroxide dissolves the precipitate, giving a liquid which soon becomes turbid. By boiling the solution, or by the addition of ammonium chloride, the indium separates as hydroxide. Ammonia does not dissolve it. *Alkali carbonates* precipitate a white, gelatinous carbonate, which, when recently thrown down, dissolves in ammonium carbonate, but not in potassium or sodium carbonate. If the solution in ammonium carbonate is boiled, the indium carbonate separates again. *Sodium phosphate* throws down a white, bulky precipitate. *Alkali-metal oxalates* produce a crystalline precipitate in concentrated, neutral solutions. *Sodium acetate* added to the nearly neutral solution of the sulphate throws down, on boiling, a basic sulphate. On digestion in the cold, *barium carbonate* precipitates the whole of the indium in the form of basic salt. (Means of separating indium from zinc, manganese, cobalt, nickel, and ferrous compounds.) From neutral or acetic acid solutions (even in the presence of a large excess of acetic acid), *hydrogen sulphide* precipitates all the indium as yellow indium sulphide. Solutions made strongly acid with mineral acids, if moderately concentrated, are not precipitated, but by large dilution with water, indium sulphide separates. Hydrogen sulphide in alkaline solutions, and *ammonium sulphide* in neutral solutions, produce a white precipitate (perhaps a compound of indium sulphide with hydrogen sulphide). If yellow indium sulphide is boiled with yellow ammonium sulphide, it also becomes white, and is partly dissolved. Upon cooling, white, voluminous indium sulphide (?) separates from the solution. *Potassium ferrocyanide* produces a white precipitate. *Potassium ferricyanide*, *sulphocyanide*, and *dichromate* give no precipitates. *Potassium chromate*, however, produces a yellow precipitate. *Zinc* precipitates the metal in the form of white, shining laminæ. Indium compounds produce a peculiar bluish-violet tinge in a *colorless flame*. The *spectrum* has two characteristic blue lines (see the spectrum plate). They appear brightest, especially α, with the chloride, but they

are very transient. For obtaining more persistent lines, the sulphide is the most suitable compound.

§ 132.

4. Gallium, Ga. (*Oxide*, Ga_2O_3.)

Up to the present time, gallium has been found only in some zinc blendes, and in very small amount. The metal is white; in the molten condition, silver-white; upon cooling, crystalline, bluish-white, and duller. It fuses at 30.16°, and its specific gravity is 5.956. It is hard, but slightly malleable, unchanged in the air at ordinary temperatures, and even when heated to redness is but little oxidized, and not volatilized. Water, even when boiling, is not decomposed by metallic gallium. In the cold, gallium is not noticeably attacked by nitric acid, but upon heating, it dissolves, with the evolution of red vapors. It also dissolves readily in hydrochloric acid, potassium hydroxide, and ammonia, with the evolution of hydrogen. Gallium oxide, Ga_2O_3, and gallium hydroxide are white. When the oxide is heated in a stream of hydrogen to a red heat, it sublimes with partial reduction, probably forming a lower oxide. Gallium salts are colorless or white. The sulphate and the nitrate dissolve in water easily, and are decomposed by ignition. Gallium sulphate combines with ammonium sulphate to form an alum. From solutions of the sulphate and also of the alum, a basic salt separates upon boiling. Gallium combines with chlorine to an easily oxidizable chloride, $GaCl_2$, and to a chloride, $GaCl_3$, corresponding to the oxide. The latter chloride is a colorless, deliquescent mass, melting at 75.° and boiling at 215°–220°. The volatility of gallium chloride shows itself even in the evaporation of hydrochloric acid solutions, but if sulphuric acid is added to them, no loss of gallium takes place, either upon evaporating the solution or upon heating the residue to a dark red heat (Lecoq de Boisbaudran). From aqueous solutions of gallium salts, the *alkalies* precipitate a white, flocculent hydroxide, which is easily soluble in an excess of the precipitant; but if a solution supersaturated with ammonia is boiled for a considerable time, all the gallium is precipitated as hydroxide. Tartaric acid prevents the precipitation by ammonia. *Alkaline carbonates* produce white precipitates, and that produced by ammonium carbonate dissolves in an excess of the precipitant. *Barium carbonate* precipitates the gallium completely, even in the cold. *Hydrogen sulphide* does not give a precipitate in gallium solutions which are made acid with hydrochloric acid; but, on the other hand, in solutions containing both free acetic acid and ammonium acetate, it produces a white precipitate of gallium sulphide. *Ammonium sulphide* also precipitates white gallium sulphide, which is insoluble in an excess of the precipitant. Tartaric acid prevents the precipitation. From dilute solutions made acid with acetic acid, upon boiling, ammonium acetate precipitates almost all the gallium, but *only* when the precipitant is not used

in too large amount. *Potassium ferrocyanide* produces a precipitate which has a bluish color (probably on account of a contamination with iron), and which is less soluble in hydrochloric acid than in water (very delicate reaction). Gallium compounds show a *spectrum* consisting of two violet lines (between G and H). The spectrum is not very distinct except as a spark-spectrum. If a gallium compound is brought into the flame of the BUNSEN burner, only one indistinct line is to be observed.

§ 133.

5. VANADIUM, V.

Vanadium occurs rarely in the form of vanadates, occasionally in small quantities in iron and copper ores, and in the slags obtained by smelting the same. There are four oxides of vanadium: vanadious oxide, VO; the sesquioxide, V_2O_3; the dioxide, VO_2; and vanadic acid, V_2O_5. Vanadious oxide is gray, possesses metallic luster, is insoluble in water, but is soluble in dilute acids, with evolution of hydrogen, to blue fluids which bleach organic coloring matters by reducing them. The sesquioxide is black, insoluble, not reduced by ignition in hydrogen, and when exposed to the air is gradually converted into the dioxide. Acid solutions of the sesquioxide are green. Vanadium dioxide is dark blue, and acid solutions of it are pure blue. All the lower oxides pass into vanadic acid, on heating with nitric acid or aqua regia, on fusing with potassium nitrate, or on igniting in oxygen or air. Vanadic acid is non-volatile, fusible, and solidifies to a crystalline mass of a dark red to orange-red color. Heated to redness in a current of hydrogen, it is changed to the sesquioxide. By exposure to moist air, anhydrous vanadic acid is converted into the dark red hydroxide. In contact with a little water, it forms a pasty mass, which dissolves in a large amount of cold water, but more readily in warm water to a blood-red liquid (A. DITTE). Vanadic acid reddens moist litmus-paper strongly, and combines with acids and with bases.

α. Acid Solutions.—The stronger acids dissolve vanadic acid to red or yellow liquids, which gradually turn green in the air (evidently on account of reducing dust). If ammonia is slowly added to a cold, acid solution of vanadic acid, the liquid becomes continually more distinctly yellow up to the moment when the reaction becomes alkaline (CARNOT). If *zinc* is introduced into the warm, dilute sulphuric acid solution, the color goes at first through green to blue (reduction to dioxide), then through greenish-blue to green (reduction to sesquioxide), and finally through violet to lavender-blue (reduction to vanadious oxide). From the lavender-blue solution, ammonia precipitates brown, readily oxidized vanadious-vanadic hydroxide. *Sulphurous acid, hydrogen sulphide, oxalic acid*, etc., also reduce acid solutions of vanadic acid, but only to the dioxide, and therefore the solutions become only blue. In the case of hydrogen sulphide, the reduc-

tion is accompanied with the separation of sulphur. When vanadic acid is boiled with concentrated hydrochloric acid, chlorine is given off, and an oxide or a corresponding chloride is formed, which is intermediate between V_2O_5 and VO_2 (ROSENHEIM). In vanadic acid solutions, *alkalies* produce brown precipitates, which are soluble in an excess of the precipitants, giving solutions of a yellowish-brown color. *Ammonium sulphide* produces a brown precipitate of vanadium sulphide, V_2S_5, which dissolves rather difficultly in an excess to a reddish-brown liquid. From this, acids precipitate brown vanadium sulphide. *Potassium ferrocyanide* throws down a green, flocculent precipitate which is insoluble in acids. In solutions which contain but little free acid, *tannic acid* produces a bluish-black precipitate. If an alkaline carbonate is added to an acid solution of vanadic acid until the free acid is almost completely neutralized, and then *mercurous nitrate* and an excess of precipitated mercuric oxide, the vanadic acid is completely precipitated as mercurous vanadate. By igniting the precipitate, vanadic acid is obtained.

β. Vanadates (with vanadic acid as the acid).—Vanadic acid forms ortho-, pyro-, and metavanadates. The vanadium minerals generally contain ortho salts. When their solutions are allowed to stand, the orthovanadates soluble in water, and those insoluble in water upon the addition of acid, are converted into pyro- and metavanadates. Alkaline pyrovanadates also easily yield metavanadic acid, even by leading carbonic acid into their solutions. Alkali-metal metavanadates are obtained by dissolving vanadic acid in potassium or sodium hydroxide, also by fusing vanadic acid with alkaline carbonates and nitrates. The solutions are colorless. If solid *ammonium chloride* is added to the neutral or alkaline solution warmed to 30°–40°, all the vanadic acid separates as ammonium metavanadate, which is insoluble in ammonium chloride solution, crystalline and colorless, and which when ignited in oxygen gives pure vanadic acid (especially characteristic reaction). Solutions of alkaline metavanadates become red with strong acids, but after a time, colorless again. *Barium chloride* (but not strontium chloride and calcium chloride, distinction from phosphoric and arsenic acids, CARNOT), *silver nitrate*, and *lead acetate*, in solutions of alkaline metavanadates, produce yellow precipitates, which become colorless upon standing, and more quickly upon warming. Soluble *uranium salts* precipitate the vanadic acid from solutions containing ammonium acetate when they are ammoniacal (or even weakly acid with acetic acid) as ammonium uranyl vanadate, $NH_4UO_2VO_4.H_2O$ (means of separating vanadic acid from alkali and alkali-earth metals, and from manganese, zinc, and copper). From boiling solutions containing ammonia and ammonium chloride, a boiling solution of *manganous chloride* containing ammonium chloride precipitates manganese pyrovanadate, $Mn_2V_2O_7$ (means of separating vanadic acid from molybdic acid, CARNOT). In contact with *aniline hydrochloride*, the alkaline metavanadates yield the vanadium chloride corresponding to the dioxide and aniline-black. *Ammonium sulphide* acts as in the acid solutions mentioned above under *α*, as does also *tannic acid* upon the addition of acetic acid. If an acidified solu-

tion of an alkaline metavanadate is shaken with *hydrogen peroxide*, it assumes a red color, or when very dilute, a brownish rose-red color. If ether is added and the whole is shaken, the solution retains its color, the ether remaining colorless (very delicate reaction, WERTHER). An excess of hydrogen peroxide produces a partial decolorization (A. WELLER). *Borax* dissolves vanadium compounds in the inner and outer flames to clear beads. The bead produced in the outer flame is colorless, or, with large quantities of vanadium, yellow; while that produced in the inner flame has a beautiful green color, but with large quantities of vanadium, it looks brownish while hot, and turns green only on cooling. Concerning the microscopic detection of vanadium, see HAUSHOFER, p. 133; BEHRENS, Zeitschr. f. analyt. Chem., 30, 161.*

§ 134.

FIFTH GROUP.

More common metals: SILVER, MERCURY, LEAD, BISMUTH, COPPER, CADMIUM.

Rarer metals: PALLADIUM, RHODIUM, OSMIUM, RUTHENIUM.

Properties of the Group.—The sulphides are insoluble both in dilute acids and in alkali-metal sulphides.† The solutions of these metals are therefore completely precipitated by hydrogen sulphide, whether they are neutral, or contain free acid (in moderate amount) or free alkali. The fact that the solutions of the metals of this group are precipitated by hydrogen sulphide in presence of a free, strong acid, distinguishes them from the metals of the fourth group and also from the metals of all the preceding groups.

For the sake of greater clearness, the more common metals of this group are divided into two classes, as follows:

1. METALS PRECIPITABLE BY HYDROCHLORIC ACID, viz., silver, mercury in mercurous salts, lead.

2. METALS NOT PRECIPITABLE BY HYDROCHLORIC ACID, viz., mercury in mercuric salts, copper, bismuth, cadmium.

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* A full summary of the most recent articles concerning the detection and determination of vanadic acid is found in the Zeitschr. f. analyt. Chem., 32, 217–232.

† Consult, however, the paragraphs on copper and mercury, as the latter remark applies only partially to them.

Lead must be considered in both classes, since the sparing solubility of its chloride might lead to confounding it with silver and mercury in mercurous salts, without affording a means of effecting its perfect separation from the metals of the second division.

Special Reactions of the More Common Metals of the Fifth Group.

FIRST DIVISION: METALS PRECIPITATED BY HYDROCHLORIC ACID.

§ 135.

a. SILVER, Ag. (*Oxide*, Ag_2O.)

1. METALLIC SILVER is white, very lustrous, moderately hard, highly malleable, and rather difficultly fusible. It is not oxidized by fusion in the air. Nitric acid dissolves silver readily, and the metal is somewhat soluble in dilute sulphuric acid (1 : 4) upon heating, if the silver is finely divided (CARY LEA). It is insoluble in hydrochloric acid.

2. SILVER OXIDE, Ag_2O, is a grayish-brown powder, which is not altogether insoluble in water, and dissolves readily in dilute nitric acid. There is no corresponding hydroxide. Silver oxide is decomposed by heat, as is also SILVER PEROXIDE, Ag_2O_2, into metallic silver and oxygen gas.

3. The SILVER SALTS are non-volatile and usually colorless, but many of them acquire a black tint upon exposure to light. The soluble normal salts do not alter vegetable colors, and are decomposed at a red heat.

4. *Hydrogen sulphide* and *ammonium sulphide* precipitate black SILVER SULPHIDE, Ag_2S, which is insoluble in dilute acids, alkalies, and alkali sulphides, but soluble in potassium cyanide. Boiling nitric acid decomposes and dissolves this precipitate readily, with separation of sulphur.

5. *Potassium* and *sodium hydroxides* precipitate SILVER OXIDE in the form of a grayish-brown powder, which is insoluble in an excess of the precipitants, but dissolves readily in ammonia.

6. *Ammonia*, if added in very small quantity to neutral solutions, throws down SILVER OXIDE as a brown precipitate,

which readily redissolves in an excess of ammonia. Acid solutions are not precipitated.

7. *Hydrochloric acid* and *soluble metallic chlorides* produce a white, curdy precipitate of SILVER CHLORIDE, AgCl. In very dilute solutions, these reagents impart at first simply a bluish-white, opalescent appearance to the fluid; but after long standing in a warm place, the silver chloride collects at the bottom of the vessel. By the action of light, the white silver chloride loses chlorine, first acquiring a violet tint, and ultimately turning black. Silver chloride is insoluble in nitric acid, but dissolves readily in ammonia as a compound of silver chloride with ammonia, from which double compound the former is again separated by acids. Concentrated hydrochloric acid and concentrated solutions of chlorides of the alkali metals dissolve silver chloride to a very perceptible extent, more particularly upon application of heat; but the dissolved chloride separates again upon dilution. Potassium cyanide dissolves silver chloride easily. Upon exposure to heat, it fuses without decomposition, giving upon cooling a translucent, horny mass.

8. In solutions of silver salts which are not too dilute, *potassium chromate* produces a dark brownish-red precipitate of SILVER CHROMATE, Ag_2CrO_4, which is easily soluble in nitric acid, dilute sulphuric acid, and also in ammonia.

9. If a clear solution of *ferrous sulphate*, containing *tartaric acid* and an *excess of ammonia*, is added to a neutral or ammoniacal solution of a silver salt, a fine, black, pulverulent precipitate separates, even at a great dilution of the silver solution. Whether this is argentous oxide, Ag_2O, or, as the investigations of FRIEDHEIM indicate, a mixture of silver oxide and finely divided silver, contaminated with organic substances, requires further investigation. *Ferrous sulphate* alone precipitates metallic silver from neutral solutions of silver salts, in the form of a gray precipitate. This separation takes place gradually in the cold, but more quickly by heating. The separated silver is sometimes deposited in the form of a mirror upon the walls of the glass vessel.

10. If compounds of silver mixed with *sodium carbonate* are exposed on a charcoal support to the INNER *flame of the blowpipe*, white, brilliant, malleable, metallic globules are

obtained, with or without a slight, dark red incrustation of the charcoal. The metal is also readily reduced in the *stick of charcoal* (p. 34).

11. In relation to the microscopic detection of silver, see HAUSHOFER, p. 117; BEHRENS, Zeitschr. f. analyt. Chem., **30**, 138.

§ 136.

b. MERCURY, Hg, IN MERCUROUS COMPOUNDS.

(*Mercurous Oxide*, Hg_2O.)

1. METALLIC MERCURY is grayish-white, lustrous, fluid at the common temperature, solidifies at −39.4°, and boils at 360°. It dissolves in cold, dilute nitric acid to mercurous nitrate, and in the hot, concentrated acid to mercuric nitrate. It does not dissolve in hydrochloric acid, and only very difficultly even upon the addition of potassium chlorate (LECCO). Mercury vapors, if such are present even in minute traces, can be readily detected by allowing them to act upon paper which has been marked with an ammoniacal silver nitrate solution. They quickly produce a blackening of the marks, in consequence of a reduction of the silver salt which takes place (MERGET). They may be detected, also, by allowing them to act upon solution of gold chloride which is free from nitric acid. They are then absorbed, with the formation of mercuric chloride and the liberation of metallic gold. The latter separates in the form of a pellicle or in spots and streaks (BARFOED).

2. MERCUROUS OXIDE, Hg_2O, is a black powder, readily soluble in nitric acid. It is decomposed and volatilized by the action of heat. There is no corresponding hydroxide.

3. The MERCUROUS OXYGEN SALTS volatilize upon ignition, suffering decomposition in this process. Mercurous chloride and mercurous bromide volatilize unaltered. Most of the mercurous salts are colorless. The soluble normal salts redden litmus-paper. Mercurous nitrate is decomposed by addition of much water into a light yellow, insoluble basic salt and a soluble acid salt.

4. *Hydrogen sulphide* and *ammonium sulphide* produce a

black precipitate, which is insoluble in dilute acids, ammonium sulphide, and potassium cyanide. The precipitate is not mercurous sulphide, as was formerly believed, but consists of MERCURIC SULPHIDE MIXED WITH FINELY DIVIDED MERCURY. In presence of some caustic soda, sodium monosulphide dissolves this precipitate, with separation of metallic mercury, but sodium disulphide dissolves it without the separation of the metal. The solutions contain mercuric sulphide, HgS, which is precipitated upon the addition of ammonium chloride. The precipitate produced by hydrogen sulphide gives up mercury to boiling, concentrated nitric acid, with formation of a white, double mercuric compound, $2HgS.Hg(NO_3)_2$. It is readily dissolved by aqua regia.

5. *Potassium* and *sodium hydroxides* precipitate MERCUROUS OXIDE, which contains MERCURIC OXIDE and METALLIC MERCURY, and is insoluble in an excess of the precipitant. *Ammonia* in very dilute solutions produces gray, in concentrated solutions black, precipitates, which are partially dissolved with decomposition, in an excess of the precipitant. In the presence of an excess of ammonia, these precipitates are mixtures of exceedingly finely divided *mercury* and of the white precipitates produced by ammonia in solutions of the corresponding mercuric salts (LEFORT, BARFOED.)

6. *Hydrochloric acid* and *soluble metallic chlorides* precipitate MERCUROUS CHLORIDE, HgCl, as a fine powder of dazzling whiteness. Cold hydrochloric and cold nitric acids fail to dissolve this precipitate, but it dissolves, although very difficultly and slowly, upon long-continued boiling with these acids, being resolved by hydrochloric acid into mercuric chloride and metallic mercury which separates, and being converted by nitric acid into mercuric chloride and mercuric nitrate. Nitro-hydrochloric acid and chlorine-water dissolve mercurous chloride readily, converting it into mercuric chloride. Ammonia and potassium hydroxide decompose mercurous chloride, the former producing a black mixture of very finely divided METALLIC MERCURY and the so-called infusible WHITE PRECIPITATE (§ 139, 5), while the black substance produced by potassium hydroxide is MERCUROUS OXIDE mixed with finely divided MERCURY and MERCURIC OXIDE (BARFOED).

7. If a drop of a neutral or slightly acid solution of a mer-

curous salt is put on a *clean and smooth surface of copper*, and washed off after some time, the spot will afterwards, on being gently rubbed with cloth, paper, etc., appear white and lustrous like silver. The application of a gentle heat to the copper causes the METALLIC MERCURY precipitated on its surface to volatilize, and thus removes the apparent silvering.

8. When added in very dilute solution and in very small amount, *stannous chloride* produces a white precipitate of MERCUROUS CHLORIDE. By the addition of larger quantities of stannous chloride, the white precipitate forming at the first instant is converted into a gray MIXTURE OF MERCUROUS CHLORIDE AND FINELY DIVIDED MERCURY. With an excess of stannous chloride, the gray precipitate is converted into a black one of finely divided MERCURY. This may be united into globules, after allowing it to settle and decanting the liquid, by boiling it with hydrochloric acid, to which a little stannous chloride may also be added.

9. From solutions of mercurous salts which are not extremely dilute, *potassium chromate* throws down a bright red precipitate of BASIC MERCUROUS CHROMATE, $3Hg_2CrO_4.Hg_2O$, which is rather difficultly soluble in nitric acid.

10. If an intimate mixture of a dry compound of mercury with anhydrous *sodium carbonate* is introduced into a glass tube which is closed at the bottom, and covered with a layer of sodium carbonate, and the tube is then strongly heated, the mercury compound invariably undergoes decomposition, and METALLIC MERCURY is liberated, forming a gray sublimate above the heated part of the tube. By means of a lens or a microscope, the sublimate will be seen to consist of globules of metal. Larger globules may be obtained by rubbing the sublimate with a glass rod. If, after cooling, a very small fragment of iodine is brought into the vicinity of the sublimate, and a very gentle heat is applied, it is converted into a mercuric iodide coating. This is generally red at first, and in that case easily visible, but sometimes it is yellow at first, and thus less easily recognized. If the tube is allowed to stand a while, the yellow iodide changes into the red. The conversion of sublimates of mercury into iodide can also be accomplished by hanging the tube with the open end down, in a small beaker having iodine upon its

bottom, using for this purpose a perforated cardboard cover upon the beaker (NEGA).

11. In regard to the microscopic detection of mercurous compounds, see HAUSHOFER, p. 111; BEHRENS, Zeitschr. f. analyt. Chem., **30**, 151.

§ 137.

c. LEAD, Pb. (*Oxide*, PbO.)

1. METALLIC LEAD is bluish-gray, and a recently cut surface exhibits a metallic luster. It is soft, malleable, readily fusible, and evaporates at a white heat. Fused upon charcoal before the blowpipe, it forms a coating of yellow oxide on the support. Hydrochloric acid and moderately concentrated sulphuric acid act upon it but little, even with the aid of heat; but dilute nitric acid dissolves it readily, more particularly on heating.

2. LEAD MONOXIDE, PbO, is a yellow or reddish-yellow powder, appearing brownish-red while hot, and fusible at a red heat. Lead hydroxide is white. Both the oxide and hydroxide dissolve readily in nitric and acetic acids. LEAD DIOXIDE, PbO_2, is brown, is converted into lead oxide by ignition, and is not dissolved by nitric acid upon heating, but is easily dissolved in that acid upon the addition of some alcohol or sugar. The solution contains lead nitrate. MINIUM, or red lead, Pb_3O_4, may be considered as a compound of lead oxide with lead dioxide. It is red in color, and nitric acid dissolves the oxide from it, leaving the dioxide.

3. The OXYGEN SALTS OF LEAD are non-volatile, and most of them are colorless. The normal soluble salts redden litmus-paper, and are decomposed at a red heat. Only a few of the insoluble salts are decomposed by ignition, for example, lead carbonate. If lead chloride is ignited in the air, part of it volatilizes, and leaves behind a compound of lead oxide and lead chloride.

4. *Hydrogen sulphide* and *ammonium sulphide* produce black precipitates of LEAD SULPHIDE, PbS, which are insoluble in *cold* dilute acids, in alkalies and alkali sulphides, and cyanides. Lead sulphide is decomposed by hot nitric acid. It

the acid is dilute, the whole of the lead is obtained in solution as lead nitrate, and sulphur separates; but if the acid is fuming, the sulphur is also completely oxidized, and insoluble lead sulphate alone is obtained; while if the acid is of medium concentration, both processes take place, a portion of the lead being obtained in solution as nitrate, while the remainder separates as sulphate, together with the unoxidized sulphur. In solutions of lead salts containing a large excess of a concentrated mineral acid, hydrogen sulphide produces a precipitate only after the addition of water or after partial neutralization of the free acid by an alkali. If a lead solution is precipitated by hydrogen sulphide in presence of a large quantity of free hydrochloric acid, a red precipitate is occasionally formed, consisting of lead chloro-sulphide, which, however, is gradually converted by an excess of hydrogen sulphide into black lead sulphide.

5. *Potassium* and *sodium hydroxides* and *ammonia* throw down BASIC SALTS in the form of white precipitates, which are insoluble in ammonia, but soluble in potassium and sodium hydroxides. In solutions of lead acetate, ammonia (free from carbonate) does not immediately produce a precipitate, owing to the formation of soluble basic lead acetates, containing one half or one third of the normal amount of acetic acid.

6. *Sodium carbonate* throws down a white precipitate, in the cold, of normal, when boiling, of more or less basic, LEAD CARBONATE, which is not quite insoluble in a large excess of the precipitant, especially on heating, but is insoluble in potassium cyanide.

7. *Hydrochloric acid* and *soluble chlorides* produce in concentrated solutions, heavy, white precipitates of LEAD CHLORIDE, $PbCl_2$, which are soluble in a large amount of water, especially upon application of heat. Lead chloride is converted by ammonia into lead oxychloride, $PbCl_2.3PbO.4H_2O$, which is also a white powder, but almost absolutely insoluble in water. In dilute nitric and hydrochloric acids, lead chloride is more difficultly soluble than in water.

8. *Sulphuric acid* and *sulphates* produce white precipitates of LEAD SULPHATE, $PbSO_4$, which are nearly insoluble in water and dilute acids. From dilute solutions, especially from such as contain much free acid, the lead sulphate precipitates

only after some time, frequently only after a long time. It is advisable to add a considerable excess of dilute sulphuric acid, as this tends to increase the delicacy of the reaction, lead sulphate being more insoluble in dilute sulphuric acid than in water. The separation of small quantities of lead sulphate is best effected by evaporating as far as practicable on the water-bath, after the addition of the sulphuric acid, and then treating the residue with water, or, if allowable, with alcohol. Lead sulphate is slightly soluble in concentrated nitric acid. It dissolves with difficulty in boiling, concentrated hydrochloric acid, but more readily in solution of potassium hydroxide. It also dissolves pretty readily in the solutions of some ammonium salts, particularly in solution of ammonium acetate upon moderate heating, and dilute sulphuric acid precipitates it again from these solutions.

9. *Potassium chromate* produces a yellow precipitate of LEAD CHROMATE, $PbCrO_4$, which is readily soluble in potassium and sodium hydroxides, but difficultly so in dilute nitric acid, and insoluble in ammonia.

10. If a mixture of a compound of lead with *sodium carbonate* is exposed on a charcoal support to the *reducing flame of the blowpipe*, soft, malleable, METALLIC GLOBULES OF LEAD are readily produced, the charcoal becoming covered at the same time with a yellow incrustation of LEAD OXIDE. The reduction may be also readily effected by means of the stick of charcoal.

11. The *metallic incrustation*, obtained according to p. 35, is black with a brown edge; the *incrustation of oxide* is light ochre-yellow; the *incrustation of iodide* varies from the yellow of a lemon to that of the yolk of an egg; while the *incrustation of sulphide* varies from brownish-red to black, and is not dissolved by ammonium sulphide (BUNSEN).

12. Concerning the microscopic detection of lead, see HAUSHOFER, p. 25; BEHRENS, Zeitschr. f. analyt. Chem., **30**, 149.

§ 138.

Recapitulation and Remarks.—The metals of the first division of the fifth group are most distinctly characterized in their chlorides, since the different reactions of these chlorides with water and ammonia afford a simple means both of

detecting them and of effecting their separation from one another. If the precipitate containing the three metallic chlorides is boiled with a somewhat large quantity of water, or boiling water is repeatedly poured over it on the filter, the lead chloride dissolves, while the silver chloride and the mercurous chloride remain undissolved. In the aqueous solution of lead chloride, the metal may be readily detected by sulphuric acid.

If the silver and mercurous chlorides are then treated with ammonia, the mercurous chloride is converted into the black precipitate, more fully described above, which is insoluble in an excess of ammonia, while the silver chloride dissolves readily in ammonia, and reprecipitates from this solution upon addition of nitric acid. (When operating upon small quantities, it is advisable first to expel the greater part of the ammonia by heat.) If the chlorides are precipitated, however, from a solution containing very much mercurous salt and only a little silver, the silver chloride cannot be completely extracted by ammonia, and in presence of a great excess of the mercurous chloride, it may happen that all the silver chloride remains behind with the mercury residue (MOECK). If very much mercury is present, therefore, and if no silver has been found in the ammoniacal solution, the black mercury product should be ignited in a porcelain crucible under a good hood until all the mercury has volatilized. Any residue remaining is then ignited with some crystals of oxalic acid until these have been also volatilized, the residue is treated with nitric acid with the aid of heat, and this solution, after diluting somewhat with water, is tested for silver with hydrochloric acid.

For separating silver from lead, or for detecting small amounts of silver in the presence of much lead, the following methods may also be used: *a.* Add to the solution some nitric acid, and then a mixture of equal parts of ammonia and solution of hydrogen peroxide, and a little ammonium carbonate. The lead then separates from the ammoniacal liquid, as a compound of lead dioxide and monoxide, in the form of a reddish-yellow precipitate, while the silver remains in solution. If the precipitate is filtered off, the filtrate acidified with nitric acid, and a little hydrochloric acid added, the silver sepa-

rates as silver chloride (P. JANNASCH). *b.* Acidify the solution containing lead and silver with a little nitric acid, heat, add a small excess of potassium chromate or dichromate, heat further, add an excess of dilute ammonia, warm for some time, and filter. Lead chromate is then obtained upon the filter, while silver chromate is contained in the ammoniacal filtrate. If the latter is acidified with nitric acid and some hydrochloric acid is added, the silver separates as silver chloride (P. JANNASCH).*

SECOND DIVISION: COMMONLY OCCURRING METALS WHICH ARE NOT PRECIPITATED BY HYDROCHLORIC ACID.

§ 139.

a. MERCURY, Hg, IN MERCURIC COMPOUNDS. (*Oxide*, HgO.)

1. MERCURIC OXIDE, HgO, is generally crystalline, and has a bright red color, which upon reduction to powder changes to a dull yellowish-red. The oxide precipitated from solutions of mercuric nitrate or chloride forms a yellow powder. It is not quite insoluble in water, and gradually turns gray in sunlight. Upon exposure to heat, it transiently acquires a deeper tint; and at a dull red heat, it is resolved into metallic mercury and oxygen. Mercuric oxide dissolves readily in hydrochloric acid and in nitric acid.

2. The MERCURIC SALTS volatilize upon ignition; the oxygen salts suffer decomposition in this process; while mercuric chloride, bromide, and iodide volatilize unaltered. On boiling a solution of the chloride, some of the salt escapes with the steam. Most of the mercuric salts are colorless. They are very poisonous. The soluble normal salts redden litmus-paper. The nitrate and sulphate are decomposed by a large quantity of water into soluble acid and insoluble basic salts.

3. Addition of a very small quantity of *hydrogen sulphide* or of *ammonium sulphide* to mercuric salt solutions produces, after shaking, a perfectly white precipitate; addition of a

* Concerning further methods for detecting little silver in presence of much lead, compare KRUTWIG, Zeitschr. f. analyt. Chem., **22**, 428; JOHNSTONE, Chem. Centralbl., 1890, 1, 298.

somewhat larger quantity of one of these reagents causes the precipitate to acquire a yellow, orange, or brownish-red color; while an excess of the precipitant produces a black precipitate of MERCURIC SULPHIDE, HgS. This progressive variation of color from white to black, which depends on the proportion of the hydrogen sulphide or ammonium sulphide added, distinguishes the mercuric salts from all others. The white precipitate which forms at first consists of a double compound of mercuric sulphide with the still undecomposed portion of the mercuric salt (in a solution of mercuric chloride, for instance, $HgCl_2.2HgS$). The gradually increasing admixture of black sulphide causes the precipitate to pass through the several gradations of color above mentioned. Ammonium sulphide dissolves only the smallest traces of mercuric sulphide, and the least amount of mercury is dissolved when the precipitate is digested hot with yellow ammonium sulphide. Potassium hydroxide and potassium cyanide do not dissolve mercuric sulphide. Potassium sulphide and sodium sulphide in the presence of some caustic potash or soda dissolve the precipitate completely (difference from silver, lead, bismuth, and copper), but it is insoluble in potassium hydrosulphide and in sodium hydrosulphide. Ammonium chloride precipitates the mercuric sulphide from its solutions in sodium or potassium sulphide. Mercuric sulphide dissolves in potassium thiocarbonate (difference from silver, lead, bismuth, and copper). It is reprecipitated from this solution by carbonic acid (difference from palladium, ROSENBLADT). Mercuric sulphide is entirely insoluble in nitric acid, even upon boiling. By the long-continued action of hot, concentrated nitric acid, it is converted, without dissolving, into the white compound, $2HgS.Hg(NO_3)_2$. Concentrated hydrochloric acid dissolves it rather readily when hot, but more difficultly when cold, yet it is insoluble or nearly so in dilute hydrochloric acid in the cold, but upon boiling, the latter dissolves it a little. Aqua regia decomposes the precipitate and dissolves it with ease. In mercuric solutions containing a large excess of concentrated mineral acid, hydrogen sulphide produces a precipitate only after the addition of water.

4. *Potassium hydroxide*, and also *sodium hydroxide*, added in small quantity, produce in neutral or slightly acid solu-

tions of mercuric salts (but not of mercuric cyanide) a reddish-brown precipitate, which acquires a yellow tint if the reagent is added in excess. The reddish-brown precipitate is a BASIC SALT, while the yellow precipitate consists of MERCURIC OXIDE, HgO. An excess of the precipitant does not redissolve these precipitates. In very acid solutions, this reaction does not take place at all, or at least the precipitation is very incomplete. In presence of ammonium salts, potassium hydroxide produces neither reddish-brown nor yellow, but white, precipitates. The precipitate thrown down by potassium hydroxide from a solution of mercuric chloride containing an excess of ammonium chloride is of nearly the same composition as that produced by ammonia (see 5).

5. *Ammonia* causes white precipitates quite analogous to those produced by potassium or sodium hydroxide in presence of ammonium chloride. For instance, from solutions of mercuric chloride, ammonia precipitates the so-called infusible white precipitate, NH_2HgCl, which may be regarded as mercurammonium chloride, or as mercuric amido-chloride. If the solution of the mercuric salt contains very much free acid, no precipitate is produced by ammonia. The white precipitates do not dissolve in ammonia, but are easily soluble in hydrochloric acid.

6. *Stannous chloride* added in small quantity to solution of mercuric chloride, or to solutions of other mercuric salts in presence of hydrochloric acid, throws down MERCUROUS CHLORIDE: $2HgCl_2 + SnCl_2 = 2HgCl + SnCl_4$. By addition of a larger quantity of the reagent, the precipitated mercurous chloride is reduced to METAL: $2HgCl + SnCl_2 = Hg_2 + SnCl_4$. The precipitate, which was white at first, therefore now acquires a gray tint, and, after it has subsided, may be readily united into globules of metallic mercury by boiling with hydrochloric acid and a little stannous chloride.

7. If a little *galvanic element*, made from a strip of platinum foil and one of tin-foil, joined at one end with a wooden clamp, but otherwise apart from each other, is introduced into a mercuric solution acidified with hydrochloric acid, all the mercury will gradually be precipitated, chiefly upon the platinum. On removing the platinum foil, drying, rolling it up, and heating strongly in a glass tube, a sublimate

of globules of mercury will be obtained, which may be more distinctly seen under the microscope (VAN DEN BROEK*). Upon the electrolytic separation of mercury depends also the method of MAYENÇON and BERGERET,† and that of C. H. WOLFF,‡ which is to be highly recommended, but requires a special apparatus. In relation to the conversions of sublimates of mercury into the iodide, compare § 136, 10.

8. For the deposition of small traces of mercury from acidified solutions upon *metals* (gold, platinum, copper, zinc), various other methods besides the foregoing may be used. One of the most convenient of these, given by FÜRBRINGER,§ consists in bringing a little (.25 to .50 g) shredded brass-wool or imitation gold-leaf (TEUBNER‖) (which is first rolled together and then pulled apart), into the liquid, which is distinctly acidified with some hydrochloric, sulphuric, or acetic acid, and heated to 60° or 80°, and allowing it to act for five or ten minutes with frequent stirring. The metal, now amalgamated, is washed with water (in presence of organic matter, also with alcohol and ether), dried between blotting-papers, formed into the shape of a spindle, and introduced into a piece of difficultly fusible glass tube which is drawn out to a capillary tube at one end; the other end of the tube near the metal is then also drawn out into a capillary tube, and the amalgamated metal is uniformly heated, just to an incipient red heat, by rotating the tube over a quietly burning gas flame. The mercury is then deposited in both capillary ends in the form of rings. If zinc rings also form, as is often the case, these are always nearer the heated part than those of mercury. The conversion of mercury coatings into mercuric iodide coatings may be carried out according to § 136, 10.¶

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* Zeitschr. f. analyt. Chem., **1**, 512. † Pharmac. Centralhalle, **14**, 317.

‡ Pharmac. Centralhalle, **24**, 315, and **29**, 342.

§ Zeitschr. f. analyt. Chem., **17**, 526. ‖ Zeitschr. f. analyt. Chem., **19**, 199.

¶ Upon a similar basis are founded the methods of LUDWIG, who uses zinc-dust (Pharmac. Centralhalle, **22**, 436); NEGA, who precipitates with brass foil (Chem. Centralbl., 1884, p. 498); A. WOLFF and J. NEGA, FR. MÜLLER, HIELBIG, MERGET, who precipitate with copper filings, foil, or wire (Zeitschr. f. analyt. Chem., **26**, 116 and 670; Chem. Centralbl., 1888, p. 1243; Zeitschr. f. analyt. Chem., **29**, 113); K. ALT, who separates the mercury by means of a leaf of artificial gold-tinsel (Chem. Centralbl., 1887, p. 1573); ALMÉN, who

9. Mercuric salts show the same reaction as mercurous salts with metallic *copper*, and when heated with *sodium carbonate* in a glass tube.

10. The microscopic detection of mercury is carried out by observing mercuric sulphate, mercuric iodide, and also cobalt mercuric sulphocyanide. (Compare HAUSHOFER, p. 112; BEHRENS, Zeitschr. f. analyt. Chem., **30**, 151.)

§ 140.

b. COPPER, Cu. (*Cupric Oxide*, CuO.)

1. METALLIC COPPER has a peculiar red color, and a strong luster; it is moderately hard, malleable, and rather difficultly fusible. In contact with water and air, it becomes covered with a green crust of basic cupric carbonate; while upon ignition in the air, it becomes coated with cuprous and cupric oxides. In hydrochloric acid and dilute sulphuric acid, it is insoluble or nearly so when air is excluded, even upon boiling. Nitric acid dissolves the metal readily. Concentrated sulphuric acid converts it into cupric sulphate, with evolution of sulphur dioxide.

2. CUPROUS OXIDE, Cu_2O, is red, and CUPROUS HYDROXIDE is yellow, both changing to cupric oxide upon ignition in the air. On treating cuprous oxide with dilute sulphuric acid, metallic copper separates, while cupric sulphate dissolves; on treating it with hydrochloric acid, white cuprous chloride is formed, which dissolves in an excess of the acid, but is reprecipitated from this solution by water.

3. CUPRIC OXIDE, CuO, is a black powder which withstands a red heat without decomposition, but by very strong ignition it loses oxygen and is converted into cuprous oxide. Its hydroxide, $Cu(OH)_2$, is light blue. Both the oxide and hydroxide dissolve with ease in hydrochloric, sulphuric, and nitric acids.

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uses copper or brass wire (Zeitschr. f. analyt. Chem., **26**, 669). MERGET presses the amalgamated copper wire, after drying, between papers soaked with ammoniacal silver nitrate solution. Dark spots result upon the latter after a few minutes.

4. Many of the normal CUPRIC SALTS are soluble in water. The soluble salts redden litmus, and those containing volatile oxygen acids suffer decomposition when heated to gentle redness, with the exception of the sulphate, which can bear a somewhat higher temperature. They are usually white in the anhydrous state, while the hydrated salts are generally of a blue or green color, which their solutions continue to exhibit even when much diluted.

5. In alkaline, neutral, and acid solutions, *hydrogen sulphide* and *ammonium sulphide* produce brownish-black precipitates of CUPRIC SULPHIDE, CuS.* This sulphide is insoluble in dilute acids and caustic alkalies. Hot solutions of potassium and sodium sulphides take sulphur from it, but do not dissolve the copper sulphide, or dissolve it only to a very trifling extent. However, it is a little more soluble in ammonium sulphide, especially if this is very yellow and acts hot. This reagent is therefore less appropriate for separating copper sulphide from other metallic sulphides. Cupric sulphide is readily decomposed and dissolved by boiling nitric acid, but it remains altogether unaffected by boiling, dilute sulphuric acid. When freshly precipitated, it dissolves easily and completely in solution of potassium cyanide. In solutions of cupric salts which contain a very large excess of a concentrated mineral acid, hydrogen sulphide produces a precipitate only after the addition of water.

6. *Potassium* or *sodium hydroxide* produces a light blue, bulky precipitate of CUPRIC HYDROXIDE, $Cu(OH)_2$. If the solution is highly concentrated and the precipitant is added in excess, the precipitate turns brownish-black after the lapse of some time, and loses its bulkiness, even in the cold, but the change takes place immediately if the precipitate is boiled with the fluid (diluted if necessary) in which it is suspended. The blue hydroxide is thereby converted into a brownish-black hydroxide, $3CuO.H_2O$, containing less water. In a large excess of very concentrated potassium or sodium hydroxide, the light blue precipitate dissolves to a blue liquid.

7. *Sodium carbonate* precipitates HYDROUS, BASIC COPPER

* According to J. THOMSEN, the precipitate is $Cu_4S_3 + S$.

CARBONATE, $CuCO_3.Cu(OH)_2$, as a greenish-blue precipitate, which dissolves in ammonia to an azure-blue and in potassium cyanide to a colorless fluid. Upon boiling, the precipitate loses the greater part of the carbonic acid contained in it, and becomes brownish-black.

8. *Ammonia* added in small quantity to solutions of normal cupric salts produces a greenish-blue precipitate, consisting of a BASIC CUPRIC SALT. This redissolves readily, upon further addition of ammonia, to a perfectly clear fluid of a magnificent azure-blue, which owes its color to the formation of a basic COPPER-AMMONIA SALT. For instance, in a solution of cupric sulphate, excess of ammonia produces $(NH_2)_2CuO.(NH_4)_2SO_4$. In solutions containing a certain amount of free acid, ammonia produces no precipitate, but this azure-blue coloration makes its appearance the instant the ammonia predominates. The blue color ceases to be perceptible only in very dilute solutions. After the lapse of some time, potassium or sodium hydroxide produces in such blue solutions in the cold, a precipitate of blue cupric hydroxide, but upon continued boiling, all the copper is precipitated as brownish-black hydroxide. With cupric salts, ammonium carbonate shows the same behavior as ammonia.

N.B.—In the presence of non-volatile organic acids, the cupric salts are not precipitated by caustic or carbonated alkalies, the resulting alkaline solutions having a deep blue color. In presence of sugar or similar organic substances caustic alkalies produce precipitates which are soluble in excess of the precipitants, but sodium carbonate produces a permanent precipitate.

9. In moderately dilute solutions, *potassium ferrocyanide* produces a reddish-brown precipitate of CUPRIC FERROCYANIDE, $Cu_2Fe(CN)_6$, insoluble in dilute acids, but decomposed by potassium or sodium hydroxide. In very highly dilute solutions, the reagent merely produces a reddish coloration.

10. If the solution of a cupric salt is mixed with sulphurous acid or with hydrochloric acid and sodium sulphite, and *potassium sulphocyanide* is then added, CUPROUS SULPHOCYANIDE, CuCNS, is thrown down. The precipitate is pale reddish-white, and is practically insoluble in water and dilute acids.

With insufficient sulphurous acid, black cupric sulphocyanide is precipitated.

11. If 2 cc of a cold, saturated potassium bromide solution is mixed with 1 cc of pure, concentrated sulphuric acid, and a few drops of a solution containing a cupric salt are added immediately, there is formed at first above the more dense lower liquid a beautiful bluish-red zone. Upon shaking, the whole liquid is colored red. The color disappears upon the addition of water. The reaction is very delicate, and permits the detection of copper in the presence of other metals (DENIGÈS).

12. When brought into contact with concentrated solutions of salts of copper, *metallic iron* is almost immediately covered with a coating of METALLIC COPPER, yet very dilute solutions produce this coating only after some time. Presence of a little free acid accelerates the reaction. Instead of the iron a small galvanic element may be made use of, constructed from a strip of platinum foil and one of bright sheet zinc, or even of tin-foil. These are fastened together at the upper end, then a flat piece of cork is put between them, and this place is also tied. The strips are given an almost parallel position, and are put into the weakly acidified copper solution in such a manner that the part which is tied together does not dip below the surface. The copper then precipitates (in the case of very dilute solutions, only after about twelve hours) principally upon the platinum, which thereby assumes a copper-red to blackish color. The advantage of this separation of copper upon platinum consists in the fact that it can be readily dissolved in nitric acid, and the resulting solution can be subjected to further tests. For this purpose, it is almost entirely evaporated, and a few drops of water and a drop of potassium ferrocyanide solution are added. Traces of copper deposited upon platinum or iron may be confirmed by moistening them with hydrochloric acid and making a test according to 14. SALET recommends using the hydrochloric acid by moistening a bundle of fine platinum wires with it, and introducing this into the flame under the iron wire or platinum strip. The delicacy of the reaction is decidedly increased by this means.

13. If a mixture of a compound of copper with *sodium*

carbonate is exposed on a charcoal support to the *inner flame of the blowpipe*, METALLIC COPPER is obtained without incrustation of the charcoal. The reduction may be also very conveniently effected in the stick of charcoal (p. 34). The best method of freeing the copper from the particles of charcoal is to triturate the fused mass in a small mortar with water, and then cautiously wash off the charcoal powder, when the copper-red metallic scales will be left behind.

14. If copper, some alloy containing copper, a trace of a salt of copper, or even simply the loop of a platinum wire dipped in a highly dilute copper solution, is introduced into the fusing zone of the *gas flame* or exposed to the inner *blowpipe flame*, the upper or outer portion of the flame shows a magnificent emerald-green tint. Addition of hydrochloric acid to the sample considerably heightens the beauty of this extremely delicate reaction. The flame then has an azure color.

15. *Borax* readily dissolves oxides of copper in the outer gas or blowpipe flame. The beads are green while hot, and blue when cold. In the inner flame, the bead is colorless unless a very large quantity of copper is present, but when cold, it is red and opaque. In the lower reducing flame of the BUNSEN gas flame, the bead does not become reddish-brown until the addition of stannic oxide, when this change rapidly takes place, owing to the production of cuprous oxide. If a bead is introduced alternately into the lower oxidizing zone and the lower reducing zone, it becomes ruby-red and transparent.

16 In relation to the microscopic detection of copper, see HAUSHOFER, p. 87; BEHRENS, Zeitschr. f. analyt. Chem., **30**, 150.

§ 111.

c. BISMUTH, Bi. (*Oxide*, Bi_2O_3.)

1. BISMUTH has a reddish tin-white color and moderate metallic luster. It is of medium hardness, brittle, unchangeable in the air at ordinary temperatures, and melts at 264°. Fused upon a charcoal support it forms an incrustation of yellow oxide. It dissolves readily in nitric acid, but is nearly

insoluble in hydrochloric acid, and altogether so in dilute sulphuric acid. Concentrated sulphuric acid converts it into bismuth sulphate, with evolution of sulphur dioxide.

2. BISMUTH OXIDE, Bi_2O_3, is a yellow powder, which transiently acquires a deeper tint when heated. It fuses at a red heat. Bismuth hydroxide, BiOOH, is white. Both the oxide and hydroxide dissolve readily in hydrochloric, sulphuric, and nitric acids. By fusion with potassium cyanide, they yield the metal. The grayish-black BISMUTHOUS OXIDE, Bi_2O_2, and the red BISMUTHIC ACID, Bi_2O_5, are converted into bismuth oxide by ignition in the air, and by heating with nitric acid, they are converted into bismuth nitrate.

3. The BISMUTH OXYGEN SALTS are non-volatile, and those containing volatile acids are decomposed at a red heat. Bismuth chloride is volatile at a moderate heat. The bismuth salts are colorless or white if the acid causes no coloration. Some of them are soluble in water, others insoluble. The soluble salts redden litmus-paper, and are decomposed by a large quantity of water into insoluble basic salts, which separate, while the greater portion of the acid remains in solution together with some bismuth.

4. In neutral and acid bismuth solutions, *hydrogen sulphide* and *ammonium sulphide* produce black precipitates of BISMUTH SULPHIDE, Bi_2S_3, which is insoluble in dilute acids, alkalies, alkali sulphides, and potassium cyanide, but is readily decomposed and dissolved by boiling nitric acid. In solutions of salts of bismuth which contain a very considerable excess of hydrochloric or nitric acid, hydrogen sulphide produces a precipitate only after the addition of water.

5. *Potassium hydroxide*, *sodium hydroxide*, and *ammonia* throw down BISMUTH HYDROXIDE, BiOOH, as a white precipitate, which is insoluble in an excess of the precipitant. If a little *hydrogen peroxide* is added to the liquid containing an excess of the precipitant, the white precipitate is converted upon warming into a yellow one of BISMUTHIC ACID. By this means, the reaction is made more delicate (HASEBROEK).

6. *Sodium carbonate* and *ammonium carbonate* throw down BASIC BISMUTH CARBONATE, $Bi_2O_2CO_3$, as a white, bulky precipitate, which is insoluble in excess of the precipitant, and in potassium cyanide. Warming assists the precipitation.

7. *Potassium dichromate* precipitates BASIC BISMUTH CHROMATE, $Bi_2O(CrO_4)_2$, as a yellow powder. This substance differs from lead chromate in being readily soluble in dilute nitric acid, and insoluble in potassium or sodium hydroxide.

8. *Dilute sulphuric acid* fails to precipitate moderately dilute solutions of bismuth nitrate. On evaporating with an excess of sulphuric acid on the water-bath until no more acid vapors escape, a white, saline mass of bismuth sulphate, $Bi_2(SO_4)_3$, is left, which always dissolves readily to a clear fluid in water acidified with sulphuric acid (characteristic difference between bismuth and lead). After long standing (several days occasionally), a basic bismuth sulphate, $Bi_2O(SO_4)_2.3H_2O$, separates from this solution in white, microscopic, needle-shaped crystals, which dissolve in nitric acid.

9. The reaction which more particularly characterizes bismuth is the decomposition of its normal salts by *water*, which is attended with the separation of insoluble basic salts. The addition of a large amount of water to solutions of bismuth salts causes the immediate formation of a dazzling white precipitate, *provided there is not too much free acid present*. This reaction is most sensitive with bismuth chloride, as the BASIC BISMUTH CHLORIDE or oxychloride, BiOCl, is almost absolutely insoluble in water. Where water fails to precipitate nitric acid solutions of bismuth, owing to the presence of too much free acid, a precipitate will almost invariably make its appearance immediately upon addition of solution of sodium chloride or ammonium chloride. Presence of tartaric acid does not interfere with the precipitation of bismuth by water.

10. On mixing a solution of bismuth with an excess of solution of *stannous chloride in potassium or sodium hydroxide*, a black precipitate of BISMUTHOUS OXIDE, Bi_2O_2, will fall. This is a very characteristic and delicate reaction: $Bi_2O_3 + K_2SnO_2 = Bi_2O_2 + K_2SnO_3$.

11. If a mixture of a compound of bismuth with *sodium carbonate* is exposed on a charcoal support to the *reducing flame*, brittle GLOBULES OF BISMUTH are obtained, which fly into pieces under the stroke of a hammer. The charcoal becomes covered at the same time with a slight incrustation of BISMUTH OXIDE, which is orange-colored while hot, and yellow

when cold. The reduction may be also conveniently effected in the stick of charcoal (p. 34). On triturating the end of the charcoal stick containing the reduced metal, yellowish spangles will be obtained.

12. The METALLIC COATING of bismuth obtained according to p. 35 is black with a brown border; the OXIDE COATING is yellowish-white, but becomes black with stannous chloride and sodium hydroxide (compare 10,—distinction from lead oxide coating); the iodide coating is bluish-brown with a red border, transiently disappearing when breathed upon; while the sulphide coating is umber-brown with a coffee-brown border, and is not removed by ammonium sulphide (BUNSEN).

13. If a compound of bismuth is heated (in case it is free from sulphur) with a mixture of equal parts of *potassium iodide* and *flowers of sulphur*, upon charcoal, before the blowpipe (if the substance already contains sufficient sulphur for the decomposition of the potassium iodide, then potassium iodide alone suffices), there is formed a very volatile, scarlet coating of bismuth iodide. When treated in the same way, compounds of lead yield a deep yellow coating, and their presence does not interfere with the bismuth reaction (v. KOBELL). The reaction also succeeds by heating the mixture in a glass tube open at both ends (CORNWALL).

14. Regarding the microscopic detection of bismuth, see HAUSHOFER, p. 138; BEHRENS, Zeitschr. f. analyt. Chem., **30**, 162.

§ 142.

d. CADMIUM, Cd. (*Oxide*, CdO.)

1. METALLIC CADMIUM has a tin-white color, is lustrous, not very hard, and is malleable. It fuses at 315° to 316°, boils at about 770°, and may therefore be sublimed in a glass tube. Heated on charcoal before the blowpipe, it takes fire and burns, emitting brown fumes of cadmium oxide, which form a coating on the charcoal. Hydrochloric acid and dilute sulphuric acid dissolve it, with evolution of hydrogen, but nitric acid dissolves it most readily.

2. CADMIUM OXIDE, CdO, is a fixed powder of a brown

color, sometimes lighter and sometimes darker in shade; but its HYDROXIDE is white. Both dissolve readily in hydrochloric, nitric, and sulphuric acids.

3. The CADMIUM SALTS are colorless or white when their acids produce no coloration, and some of them are soluble in water. The soluble normal salts redden litmus-paper, and those containing volatile oxygen acids are decomposed at a red heat.

4. In alkaline, neutral, and acid solutions, *hydrogen sulphide* and *ammonium sulphide* produce bright yellow precipitates of CADMIUM SULPHIDE, CdS, which are insoluble in dilute acids, alkalies, alkali-metal sulphides, and potassium cyanide (difference from copper). They are readily decomposed and dissolved by boiling nitric acid, as well as by boiling hydrochloric acid and by boiling dilute sulphuric acid (difference from copper). In solutions of cadmium containing a large excess of acid, hydrogen sulphide produces a precipitate only after dilution with water. By the action of hydrogen sulphide upon moderately acid, hot solutions, orange-yellow to dark red cadmium sulphide is precipitated.

5. *Potassium* and *sodium hydroxides* produce white precipitates of CADMIUM HYDROXIDE, $Cd(OH)_2$, which are insoluble in an excess of the precipitants.

6. *Ammonia* likewise precipitates white CADMIUM HYDROXIDE, which, however, redissolves readily and completely to a colorless fluid in an excess of the precipitant. The ammoniacal solution becomes turbid upon boiling, and also by diluting with much water, but this happens only when no ammonium salts are present. Potassium hydroxide as well as sodium hydroxide precipitate cadmium hydroxide from the ammoniacal solution.

7. *Sodium carbonate* and *ammonium carbonate* produce white precipitates of CADMIUM CARBONATE, $CdCO_3$, which are insoluble in an excess of sodium carbonate, and very slightly soluble in an excess of ammonium carbonate. The presence of ammonium salts impedes and interferes with the precipitation in the cold, but the precipitate is formed upon heating; and free ammonia hinders it. The precipitate is readily soluble in potassium cyanide. It separates slowly from dilute solutions, but warming assists the separation greatly.

8. *Potassium sulphocyanide* does not cause a precipitate in solutions of cadmium, even after the addition of sulphurous acid (difference from copper).

9. If a mixture of a compound of cadmium with *sodium carbonate* is exposed on a charcoal support to the *reducing flame*, the charcoal becomes covered with a deep yellow to reddish-brown coating of CADMIUM OXIDE, owing to the instant volatilization of the reduced metal and its subsequent reoxidation in passing through the oxidizing flame. The coating is seen most distinctly after cooling.

10. The *metallic incrustation*, obtained according to p. 35, is black with a brown edge; the *incrustation of oxide* is brownish-black, the edge passing from brown to white; the *incrustation of iodide* is white; while the *incrustation of sulphide* is lemon-yellow, and is not dissolved by ammonium sulphide (BUNSEN).

11. Concerning the microscopic detection of cadmium, see HAUSHOFER, p. 52; BEHRENS, Zeitschr. f. analyt. Chem., **30**, 143.

§ 143.

Recapitulation and Remarks.—As already stated, the perfect separation of the metals of the second division of the fifth group from silver and mercurous salts may be effected by means of hydrochloric acid, but this agent fails to separate them completely from lead. Traces of mercuric salt, which are at first retained by the precipitated silver chloride by surface attraction, are dissolved out completely by washing (G. J. MULDER). MERCURIC compounds are distinguished from compounds of the other metals of this division by the insolubility of mercuric sulphide in boiling nitric acid. This property affords a convenient means for its separation from copper, lead, bismuth, and to a certain extent from cadmium. Cadmium sulphide, in fact, remains behind with the mercuric sulphide partly, and if a very small quantity is present, it may remain behind wholly (BÜLOW). Care must always be taken to free the sulphides *completely* by washing from all traces of hydrochloric acid or chlorides that may happen to be present, before proceeding to boil them with nitric acid. The mercuric sulphide is readily dis-

solved by heating it with hydrochloric acid to which a very small amount of potassium chlorate is added. In a part of this solution, mercury can be detected with great ease by means of stannous chloride. The cadmium which has remained with the mercuric sulphide may be found by evaporating another portion of the solution to dryness in a porcelain crucible, and volatilizing the mercuric chloride under a good hood at a *gentle* red heat. If the residue is treated with a drop of hydrochloric acid and a little water, the cadmium is obtained in solution, and may be precipitated with hydrogen sulphide. From the remaining metals, LEAD is separated by sulphuric acid. The separation is most complete if the fluid, after addition of dilute sulphuric acid in excess, is evaporated on the water-bath, the residue diluted with water containing some sulphuric acid, and the undissolved lead sulphate filtered off immediately. The latter may be further examined in the dry way by the reaction described in § 137, 10, or also as follows: Pour over a small portion of the lead sulphate a little solution of potassium chromate, and apply heat, which will convert the white precipitate into yellow lead chromate; wash this, add a little solution of potassium or sodium hydroxide and heat; the precipitate will now dissolve to a clear fluid, and by acidifying this with acetic acid, a yellow precipitate of lead chromate will again be produced. After the removal of mercury and lead, BISMUTH may be separated from copper and cadmium by addition of ammonia in excess, as the hydroxides of the last two metals are soluble in an excess of this agent. If the precipitate, after being filtered off, is dissolved in a drop or two of hydrochloric acid on a watch-glass, and water added, the appearance of a milky turbidity is a confirmation of the presence of bismuth. The reaction given in § 141, 10, which is based upon the production of bismuthous oxide, is also well adapted for a confirmatory test. The presence of a notable quantity of COPPER is revealed by the blue color of the ammoniacal solution; while smaller quantities are detected by evaporating the ammoniacal solution nearly to dryness, adding a little acetic acid, and then potassium ferrocyanide. The separation of copper from CADMIUM may be effected by evaporating the ammoniacal solution to a small bulk, acidifying faintly with hydrochloric acid, adding

a little sulphurous acid and potassium sulphocyanide, filtering off the cuprous sulphocyanide after allowing it to stand in a warm place, and precipitating the cadmium in the filtrate by hydrogen sulphide after the removal of any sulphurous acid still present (an unnecessarily large excess of sulphurous acid should, of course, be avoided). The separation of copper from cadmium may also be effected by acting on the sulphides with potassium cyanide, or with boiling dilute sulphuric acid (5 parts of water to 1 part of concentrated acid). In the latter methods, the solution of copper and cadmium somewhat acidified with hydrochloric acid is precipitated by hydrogen sulphide, and the precipitate is separated from the fluid by decantation or filtration, and is then washed. On treating the precipitate now with some water and a small lump of potassium cyanide, the cupric sulphide will dissolve, leaving the yellow cadmium sulphide undissolved. On the other hand, by boiling the precipitate of the mixed sulphides with dilute sulphuric acid, the cupric sulphide remains undissolved, while the cadmium sulphide is obtained in solution. Hydrogen sulphide will therefore now throw down from the filtrate, yellow cadmium sulphide (A. W. HOFMANN).*

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* In regard to the detection of small traces of mercury, see the communications of TEUBNER (Zeitschr. f. analyt. Chem., **19**, 198); BIEWEND (*ibid.*, **22**, 89); J. KLEIN (*ibid.*, **29**, 186); G. KROUPA (Chem Centralbl., 1886, p. 250). Concerning the detection of traces of copper, see WILDENSTEIN (Zeitschr. f. analyt. Chem., **2**, 9); SCHAER (*ibid.*, **9**, 100); SCHÖNN (*ibid.*, **9**, 210); BELLAMY (*ibid.*, **9**, 382); PURGOTTI (*ibid.*, **18**, 476); ENDEMANN and PROCHAZKA (*ibid.*, **21**, 265); v. KNORRE (*ibid.*, **28**, 234); H. THOMS (Pharmac. Centralhalle, 1890, p. 31). In regard to the detection of bismuth, see TRESH (Zeitschr. f. analyt. Chem., **22**, 432); E. LÉGER (*ibid.*, **28**, 347). Further, concerning the detection of these metals in the presence of organic substances, see V (detection of inorganic poisons in food, etc.), in the second division of Part II. In regard to other methods for the separation of the metals of the fifth group, see especially the communications of ROSENBLADT (Zeitschr. f. analyt Chem., **26**, 15); KOHNER (*ibid.*, **27**, 217); POLSTORFF and BÜLOW (Chem. Centralbl., 1891, **2**, 227); JANNASCH and ETZ (Zeitschr. f. analyt. Chem., **33**, 67).

Special Reactions of the Rarer Metals of the Fifth Group.

§ 144.

1. PALLADIUM, Pd. (*Palladious Oxide*, PdO.)

PALLADIUM is found in the metallic state, occasionally alloyed with gold and silver, but more particularly with or in platinum ores. It greatly resembles platinum, but is somewhat darker in color. It fuses with great difficulty. Heated in the air to dull redness, it becomes covered with a blue film, but it recovers its light color and metallic luster upon more intense ignition. It is difficultly soluble in pure nitric acid, but dissolves somewhat more readily in nitric acid containing nitrous acid. It dissolves very slightly in boiling, concentrated sulphuric acid, but is soluble in fusing potassium disulphate, and readily soluble in nitro-hydrochloric acid. There are three oxides: the suboxide, Pd_2O; palladious oxide, PdO; and palladic oxide, PdO_2. PALLADIOUS OXIDE is black, the corresponding hydroxide dark brown, and both are decomposed by intense ignition, leaving a residue of metallic palladium. PALLADIC OXIDE is black. By heating with dilute hydrochloric acid, it is dissolved to palladious chloride, $PdCl_2$, with evolution of chlorine. The PALLADIOUS SALTS are mostly soluble in water, and are brown or reddish-brown. Their concentrated solutions are reddish-brown, but their dilute solutions are yellow. From a solution of palladious nitrate containing a slight excess of acid, water precipitates a brown basic salt. The oxygen salts as well as palladious chloride, are decomposed by ignition, leaving metallic palladium behind. *Hydrogen sulphide* and *ammonium sulphide* throw down from acid or neutral solutions, black palladious sulphide, which does not dissolve in ammonium sulphide, but is soluble in potassium thiocarbonate (difference from lead, copper, bismuth), and is not precipitated from the solution by carbonic acid (difference from mercury, ROSENBLADT). It is also soluble in boiling hydrochloric acid, and readily soluble in aqua regia. From the solution of palladious chloride, *potassium hydroxide* precipitates a brown basic salt, which is soluble in a large excess of the precipitant. *Ammonia* precipitates a flesh-red compound of palladious chloride and ammonia, which is soluble in an excess of ammonia (rather rapidly by heating, slowly in the cold) to a colorless liquid from which hydrochloric acid precipitates yellow, crystalline palladammonium chloride, $Pd(NH_3)_2Cl_2$. *Mercuric cyanide* throws down from neutral or slightly acid solutions, yellowish-white palladious cyanide as a gelatinous precipitate, slightly soluble in hydrochloric acid, and readily soluble in ammonia (especially characteristic). In the absence of free hydrochloric acid, *stannous chloride* produces a brownish-black precipitate; but in presence of free hydrochloric acid, a red solution, which speedily turns brown, and ultimately green, and becomes brownish-red upon addition of water. *Sodium formate* precipitates

at 50° all the palladium in the metallic state as palladium-black. *Potassium iodide* precipitates black palladious iodide, which is soluble in an excess of the precipitant, giving a dark brown color (especially characteristic). *Potassium chloride* precipitates from highly concentrated solutions, potassium palladious chloride, $2KCl.PdCl_2$, in the form of golden-yellow needles, which dissolve readily in water to a dark red fluid, but are insoluble in absolute alcohol. *Potassium nitrite* produces in not too dilute solutions, a yellowish, crystalline precipitate, which becomes reddish on long standing, and is soluble in much water. *Potassium sulphocyanide* does not precipitate palladium, even after the addition of sulphurous acid (difference from copper, and best means of separating from the same). On treatment with *sodium carbonate* in the upper oxidizing flame (p. 32), all the compounds of palladium yield a gray, metallic sponge. When this is triturated in an agate mortar, silver-white, ductile, metallic spangles are obtained. Concerning the microscopic detection of palladium, see HAUSHOFER, p. 107; BEHRENS, Zeitschr. f. analyt. Chem., 30, 153.

§ 145.

2. RHODIUM, Rh. (*Rhodic Oxide*, Rh_2O_3.)

RHODIUM is found in small quantity in platinum ores. It is almost silver-white, malleable, and very difficultly fusible. When prepared in the wet way, it is a gray powder. Compact rhodium is insoluble in all acids. Even in aqua regia, it dissolves only when alloyed with platinum, copper, etc., and not when alloyed with gold or silver. Precipitated rhodium, on the other hand, is somewhat soluble in nitric acid and in hydrochloric acid in presence of air. Fusing metaphosphoric acid and fusing potassium disulphate dissolve it, forming rhodic salts. Heated in chlorine, it yields a chloride of variable composition (CLAUS, LEIDIÉ). Heated with potassium or sodium chloride in a stream of chlorine, double chlorides are formed. Sodium rhodic chloride is insoluble in alcohol (means of separation from platinum and other metals). There are three oxides: rhodious oxide, RhO; rhodic oxide, Rh_2O_3; and the dioxide, RhO_2. RHODIC OXIDE is gray or black, and yields a yellow and a brownish-black hydroxide. It is insoluble in acids, but dissolves in the fluxes mentioned in connection with the metal. The solutions have a beautiful red color. Upon prolonged action, especially by the aid of heat (but even then complete precipitation is difficult), *hydrogen sulphide* precipitates brown rhodium sulph-hydrate, $Rh_2(SH)_6$, which is not dissolved by acids or alkali-metal sulphides, but is easily soluble in bromine and aqua regia. When it is boiled with much water, it is decomposed into rhodium sulphide and hydrogen sulphide, with contraction in volume. Normal *alkali-metal sulphides* precipitate compounds of rhodium sulphide with alkali-metal sulphides in the form of brownish-black precipitates, which are insoluble in an excess

of the precipitant, and are decomposable by water (LEIDIÉ). *Potassium hydroxide*, added in not too great excess to solutions of rhodic oxygen salts, produces immediately a yellow precipitate of the hydroxide, $Rh(OH)_3.H_2O$, which is soluble at the ordinary temperature in an excess of potassium hydroxide, and by boiling the yellow solution, the blackish-brown hydroxide, $Rh(OH)_3$, is precipitated. In solutions of rhodic chloride, no precipitation is produced at first by potassium hydroxide, but upon the addition of alcohol, a black hydroxide soon separates (CLAUS). *Ammonia* produces, after some time, a yellow precipitate, soluble in hydrochloric acid. *Zinc* precipitates black metallic rhodium. Upon heating with *potassium nitrite*, a solution of rhodic chloride becomes yellow and an orange-yellow powder separates, which is but little soluble in water, although easily soluble in hydrochloric acid; while at the same time, another part of the rhodium is converted into a yellow salt, soluble in water, which may be precipitated by alcohol. The insolubility of potassium rhodic nitrite in alcohol permits a separation of rhodium from ruthenium (GIBBS). If a slight excess of a freshly prepared solution of sodium hypochlorite is added to a not too dilute, neutral, or weakly acid solution of ammonium rhodium chloride, a yellowish precipitate is obtained. If dilute acetic acid (1 : 5) is now added drop by drop, with continual stirring, the precipitate dissolves, and the liquid assumes an intense orange color; then it quickly becomes decolorized, gives a gray precipitate, and finally an intense sky-blue color (DEMARÇAY). On ignition in *hydrogen*, or on ignition on a platinum wire with *sodium carbonate* in the upper oxidizing flame, all solid compounds of rhodium yield the metal, which is well characterized by its insolubility in aqua regia, and its solubility in fusing potassium disulphate. The fused mass obtained with the latter is yellow after cooling, and dissolves in water with a yellow color. By adding hydrochloric acid, the solution becomes red (BUNSEN). The microscopic detection of rhodium depends upon an examination of potassium rhodic nitrite, of rhodic oxalate (BEHRENS, Zeitschr. f. analyt. Chem., **30**, 154), or of ammonium rhodic chloride (WILM, Ber. der deutch. chem. Gesellsch., 1885, p. 2547).

§ 146.

3. OSMIUM, Os.

OSMIUM is found rarely in platinum ores as a native alloy of osmium and iridium, etc. It is generally obtained as a black powder, or gray with metallic luster, and is infusible. The metal, OSMIOUS OXIDE, OsO, the SESQUIOXIDE, Os_2O_3, and OSMIC OXIDE, OsO_2, oxidize readily when heated to redness in the air, and give PEROSMIC ACID, OsO_4, which volatilizes and makes its presence speedily known by its exceedingly irritating and offensive smell, resembling that of chlorine and iodine (highly characteristic). If a little osmium on a strip of platinum foil is held in the outer mantle of

a *gas or alcohol flame*, at half its height, the flame becomes most strikingly luminous. By this reaction, even minute traces of osmium may be detected in alloys of iridium and osmium, but the reaction in that case is only momentary, still it may be reproduced by holding the sample first in the reducing flame, and then again in the outer mantle. *Nitric acid*, more particularly red fuming nitric acid, and aqua regia dissolve osmium to perosmic acid. Application of heat promotes the solution, which is, however, attended with volatilization of perosmic acid. Very intensely ignited osmium is insoluble in acids. On fusing with potassium nitrate and distilling the dissolved mass with nitric acid, perosmic acid is found in the distillate (characteristic reaction for all osmium compounds). By heating osmium in dry *chlorine* free from air, bluish-black OSMIOUS CHLORIDE, $OsCl_3$, is first formed, but always only in small quantity, then the more volatile and red OSMIC CHLORIDE, $OsCl_4$; while if moist chlorine is used, a green mixture of both chlorides is formed. The osmious chloride dissolves with a blue color, the osmic chloride with a yellow color, and both together with a green color, which turns red. The solutions are soon decomposed, perosmic acid, hydrochloric acid, and a mixture of osmious and osmic oxides being formed, while the mixed oxides separate as a black powder. On heating a mixture of powdered osmium or osmium sulphide and potassium chloride, in chlorine, a double salt, POTASSIUM OSMIC CHLORIDE, is produced, which is somewhat difficultly soluble in cold water, but more readily so in hot water. From the yellow solution, alcohol precipitates the salt as a red, crystalline powder. Potassium hydroxide precipitates a black hydroxide upon heating. Upon fusing potassium osmic chloride with sodium carbonate, blackish-gray osmic oxide, insoluble in water and in hydrochloric acid, is formed. The double salt, $3KCl.OsCl_3.3H_2O$, dissolves in water very easily. The deep cherry-red solution is decomposed readily, especially when warm, with separation of black oxychloride. Potassium hydroxide precipitates from this solution a reddish-brown hydroxide. Anhydrous PEROSMIC ACID is white, crystalline, fusible at a gentle heat, and boils at about 100°. The fumes possess an unendurable odor, and attack the nose and eyes powerfully. Heated with water it fuses and dissolves slowly. The solution is colorless, gives no acid reaction, and has a strong, irritating, unpleasant smell. Concentrated potassium hydroxide solution colors the solution yellow, and upon distilling, the greater part of the osmium passes over as perosmic acid (very characteristic), the remainder gives off oxygen, forming potassium osmate, K_2OsO_4, and upon continued boiling forms perosmic acid, osmic hydroxide, and potassium hydroxide. Perosmic acid decolorizes *indigo solution*, separates iodine from *potassium iodide*, and converts *alcohol* into aldehyde and acetic acid. *Potassium nitrite* readily reduces it to potassium osmate, which separates out in garnet-red crystals. *Hydrogen sulphide* colors the aqueous solution of perosmic acid dark brown, and upon the addition of acid, a dark brown precipitate of osmium sulphide is produced, which is insoluble in alkaline hydroxides and carbonates, as well as in ammonium and alkali-metal sulphides. *Sulphurous acid*, added in increasing amount, produces a yellow,

reddish-brown, green, and finally an indigo-blue color. *Ferrous sulphate* causes a black precipitate of osmic oxide. *Stannous chloride* gives a brown precipitate, soluble in hydrochloric acid to a brown fluid. *Zinc* and many other metals, in the presence of a strong acid, precipitate metallic osmium. All the compounds of osmium yield the metal on ignition in a current of *hydrogen;* but upon ignition in the *oxidizing flame*, volatile perosmic acid is formed, recognizable by its odor, etc. Concerning the microscopic detection of osmium, compare BEHRENS, Zeitschr. f. analyt. Chem., 30, 154.

§ 147.

4. RUTHENIUM, Ru.

RUTHENIUM is found in small quantity in platinum ores. It is a grayish-white, brittle, and exceedingly difficultly fusible metal. The powder is grayish-black. It is barely acted upon by aqua regia, and fusing potassium disulphate fails altogether to affect it. It combines with oxygen, forming ruthenious oxide, RuO, the sesquioxide, Ru_2O_3, ruthenic oxide, RuO_2, ruthenic acid, RuO_3 (only known in compounds), and perruthenic acid, RuO_4. By ignition in the air, the pulverulent metal forms the black sesquioxide,* which is insoluble in acids.

By ignition of the metal mixed with potassium chloride in a stream of chlorine, the double salt, $2KCl.RuCl_3$, is formed, which dissolves in water with an orange-yellow color. From the solution, there separates gradually upon standing, but at once upon heating, a black, voluminous precipitate, which remains suspended for a long time, and has the property of staining very strongly (delicate reaction). *Potassium hydroxide, sodium hydroxide*, and also *ammonia* throw down the blackish-brown, hydrated sesquioxide, which is insoluble in an excess of the fixed alkalies, but is soluble in an excess of ammonia, with a greenish-brown color, and dissolves in hydrochloric acid to an orange-colored solution. *Hydrogen sulphide* produces, only after some time, a light-colored precipitate, perhaps a mixture of black ruthenium sulphide and sulphur. The precipitate gradually becomes darker, while the liquid assumes a deep blue color. *Ammonium sulphide* gives a brownish-black precipitate, which is scarcely soluble in an excess of the precipitant. *Zinc* gives at first an indigo-blue color, in consequence of a reduction from ruthenic to ruthenious chloride, and afterwards metallic ruthenium is deposited. *Potassium sulphocyanide* produces (in absence of other metals of platinum ores) after some time, a red coloration, gradually becoming purplish-red, and upon heating, a beautiful violet coloration (very characteristic). *Potassium iodide* precipitates gradually in the cold, but at once upon heating, black ruthenic

*According to DEBRAY and JOLY, the product thus obtained is, in all probability, only a mixture of ruthenic oxide with metallic ruthenium.

iodide. If *potassium nitrite* is added to the solution which is made weakly alkaline with sodium carbonate, it is then heated to boiling, allowed to cool, and a very little colorless ammonium sulphide is added, the liquid becomes colored a beautiful crimson-red, afterwards brown (even in the presence of other metals occurring in the platinum ores). More ammonium sulphide produces a brown precipitate. If to a solution of *sodium thiosulphate* containing ammonia, a few drops of a solution of ruthenium trichloride are added, the liquid assumes an intense purple-red color.

Ruthenic oxide is a blackish-blue powder, insoluble in acids, and dissolving in fusing potassium hydroxide with a brown color. Its hydroxide has a dark ochre color, and is soluble in acids to light yellow liquids. By fusing metallic ruthenium with potassium hydroxide and potassium nitrate or chlorate, an orange-red mass results, containing *potassium ruthenate*, which dissolves in water, forming an orange-yellow solution. It colors organic bodies black. Acids or alcohol precipitate from it the hydrated sesquioxide. *Perruthenic acid* forms a yellow, crystalline mass, which evaporates even at the ordinary temperature. It fuses easily, and boils somewhat above 100°. The golden-yellow gas has an odor similar to that of nitrous acid. Perruthenic acid dissolves slowly and difficultly in water. Upon being heated with *hydrochloric acid*, ruthenium sesquichloride is formed, with evolution of chlorine. *Sulphurous acid* colors it purple-red at first, then violet-blue. *Hydrogen sulphide* precipitates a black oxysulphide, with a transitory red coloration of the liquid. In relation to the microscopic detection of ruthenium, see BEHRENS, Zeitschr. f. analyt. Chem., 30, 154.

§ 148.

SIXTH GROUP.

More common metals: GOLD, PLATINUM, TIN, ANTIMONY, ARSENIC.

Rarer metals: GERMANIUM, IRIDIUM, MOLYBDENUM, TUNGSTEN, TELLURIUM, SELENIUM.

The higher oxides of the elements belonging to the sixth group all have more or less strongly pronounced acid characters. They are included here, however, as they cannot well be separated from the lower oxides of the same elements, to which they are very closely allied in their reactions with hydrogen sulphide.

Properties of the Group.—The sulphides of the metals of the sixth group are insoluble in dilute acids. These sulphides combine with alkali-metal sulphides (either directly, or with

the addition of sulphur) to soluble sulphur salts, in which they take the part of the acid. From acidified solutions, therefore, hydrogen sulphide precipitates these elements completely, like those of the fifth group. The precipitated sulphides differ, however, from those of the fifth group in this, that they dissolve in ammonium sulphide, potassium sulphide, etc., and are precipitated from these solutions by the addition of acids.

The more common metals of this group are divided into two classes, as follows:

1. The noble metals, GOLD and PLATINUM. Their oxides are decomposed by ignition into the metal and oxygen, and their chlorides, into the metal and chlorine. The precipitates formed by hydrogen sulphide, especially if the precipitations have been made from hot solutions, are not soluble in boiling hydrochloric acid, and dissolve scarcely or not at all in boiling nitric acid. The sulphides are more difficultly soluble in alkali-metal sulphides, especially in ammonium sulphide, than are the sulphides of the ignoble metals of this group. When heated in a stream of chlorine, or with a mixture of 5 parts of ammonium chloride and 1 part of ammonium nitrate, the sulphides give the metals.

2. The ignoble metals, TIN, ANTIMONY, and ARSENIC. The oxides of these elements are not decomposed into metal and oxygen by ignition, and their chlorides are volatile upon heating. The sulphides dissolve in boiling hydrochloric acid (with the exception of the sulphides of arsenic), and are dissolved or decomposed by boiling nitric acid. When ignited in a stream of chlorine, or with a mixture of 5 parts of ammonium chloride and 1 part of ammonium nitrate, the sulphides are completely volatilized.

FIRST DIVISION.

Special Reactions.

§ 149.

a. GOLD, Au. (*Auric Oxide*, Au_2O_3.)

1. METALLIC GOLD has a yellow color, a very high luster, is rather soft, and exceedingly malleable. When precipi-

tated in the form of powder, it is brown and dull. It is difficultly fusible, does not oxidize upon ignition in the air, and is insoluble in hydrochloric, nitric, and sulphuric acids. It dissolves somewhat in hot concentrated sulphuric acid containing nitric acid, and readily in fluids containing or evolving chlorine, *e.g.*, in nitro-hydrochloric acid. The solutions contain auric chloride. Liquids which contain free bromine and iodine also dissolve gold. Fusing potassium disulphate does not attack it. Alkali-metal hydroxides with access of air, and also the nitrates, oxidize it at the temperature of fusion. It dissolves slowly in potassium cyanide solution, with access of air.

2. AURIC OXIDE (Au_2O_3) is a blackish-brown, and its hydroxide is an ochre-brown or also a blackish-brown, powder. Both are reduced by light and heat, and dissolve readily in hydrochloric acid, but not in dilute oxygen acids. Concentrated nitric and sulphuric acids dissolve a little auric oxide, but water reprecipitates it from these solutions. AUROUS OXIDE, Au_2O, is violet-black, and is decomposed by heat into gold and oxygen.

3. OXYGEN SALTS of gold are practically unknown. AURIC CHLORIDE, $AuCl_3$, is red to brownish-red, loses chlorine at 150° to 200°, and leaves yellowish-white AUROUS CHLORIDE, AuCl, which is decomposed by stronger heating into chlorine and gold, and by treatment with water, into metallic gold and auric chloride. Auric chloride solution is brownish-red when concentrated, and reddish-yellow when more dilute. It shows a yellow coloration to a great degree of dilution. Solution of auric chloride reddens litmus. Hydrogen gold chloride (hydrochlorauric acid), $HCl.AuCl_3.4H_2O$, crystallizes in light yellow crystals, which with water give a bright yellow solution, the so-called acid gold chloride solution.

4. *Hydrogen sulphide* precipitates the whole of the metal from neutral or acid solutions. The brownish-black precipitate, when precipitated cold, is GOLD SULPHIDE, Au_2S_3 (L. HOFFMANN and G. KRÜSS). Precipitated under somewhat different conditions, it is often mixed with metallic gold or sulphur (v. SCHRÖTTER and PRIWOZNIK). The precipitate is insoluble in hydrochloric and in nitric acids, even upon heating, but is soluble in nitro-hydrochloric acid. It is also soluble in

colorless and in yellow ammonium sulphide, especially by heating, and more readily still in sodium sulphide or potassium sulphide, sometimes leaving behind a residue of black, pulverulent gold. It leaves metallic gold when ignited in a stream of chlorine, or with a mixture of 5 parts of ammonium chloride and 1 part of ammonium nitrate.

5. *Ammonium sulphide* precipitates brownish-black GOLD SULPHIDE, Au_2S_3, which redissolves in an excess of the precipitant, especially upon heating.

6. *Ammonia* produces, though only in concentrated solutions of gold, reddish-yellow precipitates of AURIC OXIDE combined with AMMONIA (fulminating gold). The more acid the solution and the greater the excess of ammonia added, the more gold remains in solution.

7. *Stannous chloride*, containing an admixture of *stannic chloride* (which may be easily prepared by mixing a solution of stannous chloride with a little chlorine-water) produces, even in extremely dilute solutions of gold, a purple-red precipitate or at least coloration, which sometimes inclines rather to violet or to brownish-red. This precipitate, which has received the name of PURPLE OF CASSIUS,* is decomposed by hydrochloric acid, with the separation of gold.

8. *Ferrous salts* reduce auric chloride in its solutions, and precipitate METALLIC GOLD in the form of a most minutely divided, brown powder. The fluid in which the precipitate is suspended appears of a blackish-blue color by transmitted light. The dried precipitate shows metallic luster when pressed with the blade of a knife. If, before a small amount of ferrous sulphate solution is added, the auric chloride solution is made alkaline by a few drops of potassium or sodium hydroxide, a black precipitate is obtained instead of a dirty green one, even at a great dilution (H. ROSE, RÜDORFF).

9. *Potassium nitrite* produces, even in highly dilute solutions, a precipitate of METALLIC GOLD. In very dilute solutions,

* The much-discussed question, whether the purple of Cassius is a gold compound, or whether its color is due to metallic gold contained in it in a state of the finest division, has been decided in favor of the latter view, by the comprehensive experiments of MAX MÜLLER, Journ. f. prakt. Chem., 30, 252.

the fluid at first shows only a blue color. *Sulphurous acid* also precipitates GOLD slowly in the cold, but rapidly by heating.

10. If *oxalic acid* is added to a gold solution which is free from nitric acid, and which contains little or no hydrochloric acid or alkali-metal chloride, the GOLD separates upon warming, with evolution of carbonic acid, either in the form of brilliant scales or as a golden metallic mirror upon the surface of the glass vessel, according to the concentration of the solution: $2AuCl_3 + 3H_2C_2O_4 = 2Au + 6HCl + 6CO_2$.

11. All compounds of gold are reduced in the *stick of charcoal* (p. 34). By triturating the charcoal afterwards, yellow spangles of metal may be obtained, which are insoluble in nitric acid, but readily soluble in aqua regia.

§ 150.

b. PLATINUM, Pt. (*Platinic Oxide*, PtO_2.)

1. METALLIC PLATINUM in the compact condition has a light steel-gray color. It is very lustrous, moderately hard, very malleable, very difficultly fusible, and does not oxidize upon ignition in the air. Platinum sponge is dull gray, and precipitated platinum (platinum-black) is black and finely pulverulent. Platinum is insoluble in hydrochloric, nitric, and sulphuric acids, but dissolves in nitro-hydrochloric acid, especially upon heating. When hydrochloric acid is in excess, the solution contains hydrogen platinic chloride (hydrochloroplatinic acid). Fusing potassium disulphate does not attack platinum, but alkali-metal nitrates oxidize it at a red heat, as do also the hydroxides with access of air.

2. PLATINIC OXIDE, PtO_2, is a black powder, while PLATINIC HYDROXIDE, $Pt(OH)_4$, is a reddish-brown powder. Both are reduced by heat. The hydroxide is easily soluble in dilute acids and in sodium hydroxide. PLATINOUS OXIDE, PtO, is dark violet, its hydroxide is black, and they are both reduced by ignition to the metallic state.

3. The PLATINIC OXYGEN SALTS are decomposed by ignition. They have a yellow or a brown color. Platinic chloride, $PtCl_4.5H_2O$, forms red crystals, while hydrogen platinic chloride, $2HCl.PtCl_4.6H_2O$, forms brownish-red ones. What is

usually called platinic chloride solution is the solution of hydrogen platinic chloride (hydrochloroplatinic acid). This has an acid reaction. Platinic chloride and also hydrogen platinic chloride are converted into platinous chloride, $PtCl_2$, at a low red heat, and upon stronger ignition, into metallic platinum. A platinic chloride solution containing platinous chloride has a deep, dark brown color.

4. *Hydrogen sulphide* gradually colors acid or neutral solutions brown, and upon continued action, black PLATINIC SULPHIDE, PtS_2, is precipitated, but even after prolonged action, the precipitation is not complete. If the solution containing hydrogen sulphide is heated, the precipitate is formed at once. Many bodies precipitate with it readily, which by themselves are not precipitated in acid solutions by hydrogen sulphide, especially ferrous sulphide (WILM). Alkali-metal sulphides, particularly when containing an excess of sulphur, dissolve platinic sulphide when they are employed in large excess, and act with the aid of heat, but always very slowly, and complete solution is attained only with great difficulty. Hot nitric acid dissolves platinic sulphide which has been precipitated in the cold to a dark brown liquid, while it scarcely dissolves that which has been precipitated hot. Hydrochloric acid does not dissolve platinic sulphide, even upon heating. When it is ignited in a stream of chlorine or with a mixture of 5 parts of ammonium chloride and 1 part of ammonium nitrate, metallic platinum is left behind.

5. *Ammonium sulphide* also produces blackish-brown platinic sulphide. This redissolves slowly and with difficulty in a large excess of the precipitant (especially if the latter contains an excess of sulphur), somewhat more readily upon heating, but completely, only with difficulty. Acids reprecipitate the platinic sulphide unaltered from the reddish-brown solution.

6. *Potassium chloride* and *ammonium chloride* (and accordingly also potassium hydroxide and ammonia in presence of hydrochloric acid) produce in not too highly dilute solutions of platinic chloride, yellow, crystalline precipitates of POTASSIUM and AMMONIUM PLATINIC CHLORIDE. From dilute solutions, these precipitates are obtained by evaporating the fluid mixed with the precipitant, on the water-bath, and treating the resi-

due with a little water or with dilute alcohol. The precipitates dissolve in acids somewhat more readily than in water, and dissolve in concentrated potassium or sodium hydroxide upon warming. Upon ignition, ammonium platinic chloride leaves spongy platinum behind, while potassium platinic chloride leaves platinum and potassium chloride. The decomposition of the latter is complete only if the ignition is effected in a current of hydrogen gas, or with addition of some oxalic acid.

7. *Stannous chloride* imparts to platinic solutions containing much free hydrochloric acid, an intensely dark red to brownish-red color, owing to a reduction of platinic chloride to platinous chloride, but the reagent produces no precipitate in such solutions.

8. *Ferrous sulphate* does not precipitate solution of platinic chloride except upon very long-continued boiling, in which case, the chloride ultimately suffers reduction, with the separation of platinum. If, however, sodium hydroxide is added to the platinic chloride solution after the addition of ferrous sulphate, and hydrochloric acid is then added, PLATINUM-BLACK is precipitated.

9. If *potassium iodide* in excess is added to a solution of hydrogen platinic chloride, there is obtained a very characteristic, deep, dark red coloration, or, with very dilute solutions, a rose-red color.

10. *Oxalic acid* and *sulphurous acid* throw down no platinum from platinic chloride solutions, even upon heating.

11. On igniting a compound of platinum mixed with *sodium carbonate* on the loop of a platinum wire, in the upper *oxidizing flame*, a gray, spongy mass is obtained, which on trituration in an agate mortar yields silver-white, ductile, metallic spangles, insoluble in hydrochloric and in nitric acids, but soluble in aqua regia.

§ 151.

Recapitulation and Remarks.—The reactions of gold and platinum enable us, in many cases, to detect these two metals directly in the presence of many others, and especially in solutions containing the two metals alone. In the latter

case, it is best to evaporate the solution almost to dryness upon the water-bath, evaporating with repeated additions of hydrochloric acid if nitric acid is present. The residue is then taken up with water, oxalic acid is added to the solution (which should now contain almost no hydrochloric acid), and it is warmed for a long time, so that the gold is completely precipitated. The liquid filtered from the gold is treated with ammonium chloride, evaporated almost to dryness, and the residue is treated with weak alcohol. The excess of the ammonium chloride and oxalic acid is thus dissolved, while the platinum remains behind as ammonium platinic chloride. If very little platinum is present, it is better to evaporate the liquid filtered from the gold to dryness, and to ignite the residue in order to remove the oxalic acid. The platinum remains behind in the metallic state. This is dissolved in a few drops of aqua regia, and the resulting solution is subjected to further tests. Concerning the microscopic detection of gold and platinum, see HAUSHOFER, pp. 50 and 100; BEHRENS, Zeitschr. f. analyt. Chem., **30**, 152.

SECOND DIVISION.

Special Reactions.

§ 152.

a. TIN, Sn, AND STANNOUS COMPOUNDS. (*Stannous Oxide*, SnO.)

1. TIN has a light grayish-white color and a high metallic luster. It is soft and malleable, and when bent it produces a crackling sound. It melts at 228.5°, and boils at a white heat. Heated in the air, it is oxidized (but this takes place completely only after long heating), and is converted into white stannic oxide; and heated on charcoal before the blowpipe, it forms a white incrustation. Concentrated hydrochloric acid dissolves tin to stannous chloride, with evolution of hydrogen gas; nitro-hydrochloric acid dissolves it, according to circumstances, to stannic chloride or to a mixture of stannous and stannic chlorides. Tin dissolves with difficulty in

dilute sulphuric acid; but with the aid of heat, concentrated sulphuric acid in excess converts it into stannic sulphate. Moderately dilute nitric acid oxidizes it readily, particularly with the aid of heat; but the white hydroxide formed, metastannic acid, $Sn(OH)_4$, does not redissolve in an excess of the nitric acid.

2. STANNOUS OXIDE, SnO, is a black or grayish-black powder, while stannous hydroxide is white. Stannous oxide is reduced to metal by fusion with potassium cyanide. It is readily soluble in hydrochloric acid, but nitric acid converts it into metastannic acid, which is insoluble in an excess of the acid.

3. The STANNOUS SALTS are colorless. The oxygen salts of volatile acids are decomposed by heat, with the formation of stannic oxide where there is access of air. The soluble, normal salts redden litmus-paper, while those which are insoluble in water dissolve in hydrochloric acid, if they have not been ignited. The stannous oxygen salts rapidly absorb oxygen from the air, and are partially or entirely converted into stannic salts. Stannous chloride, whether in crystals or in solution, also absorbs oxygen from the air, which leads to the formation of insoluble stannous oxychloride and stannic chloride. Hence, a solution of stannous chloride becomes speedily turbid if the bottle is often opened, and there is only little free acid present; and none but quite recently prepared stannous chloride will completely dissolve in water free from air, while crystals of the salt that have been kept for any time will dissolve to a clear fluid only in water containing hydrochloric acid.

4. *Hydrogen sulphide* throws down from neutral and acid solutions, a dark brown precipitate of STANNOUS SULPHIDE, SnS, which contains water. This reagent does not precipitate alkaline solutions, at least not completely. The precipitation may be prevented by the presence of a very large quantity of free hydrochloric acid. The precipitate is insoluble, or nearly so, in colorless ammonium sulphide, but dissolves readily in the yellow sulphide. From this solution, acids precipitate yellow stannic sulphide mixed with sulphur. Stannous sulphide also dissolves in solutions of sodium and potassium hydroxides. Warming accelerates the complete

solution. Acids reprecipitate it unaltered from these solutions. Boiling hydrochloric acid dissolves it, with evolution of hydrogen sulphide; and boiling nitric acid converts it into insoluble metastannic acid. Stannous sulphide, when ignited in a stream of chlorine or with a mixture of 5 parts of ammonium chloride and 1 part of ammonium nitrate, is decomposed and completely volatilized. If the latter operation is performed in a glass tube closed at one end, the tin is found as stannic chloride in the sublimate.

5. *Ammonium sulphide* also precipitates hydrous STANNOUS SULPHIDE.

6. *Potassium hydroxide, sodium hydroxide, ammonia,* and *carbonates of the alkali metals* produce a white, bulky precipitate of STANNOUS HYDROXIDE, $Sn(OH)_2$, which redissolves readily in an excess of potassium or sodium hydroxide, but is insoluble in an excess of the other precipitants. If the solution of stannous hydroxide in potassium hydroxide is briskly evaporated, potassium stannate is formed, which remains in solution, while metallic tin precipitates; but upon evaporating slowly, crystalline stannous oxide separates.

7. If a few drops of *bismuth nitrate* solution are added to a solution of stannous oxide in potassium or sodium hydroxide, there results a white precipitate, which rapidly changes into black bismuthous oxide (compare § 141, 10). The reaction is very delicate.

8. In solutions of stannous chloride and in those of other stannous salts mixed with hydrochloric acid, *auric chloride* produces a precipitate which varies in color between brown, reddish-brown, and purple-red, according to the presence of more or less stannic chloride and the state of concentration (compare § 149, 7). In very dilute solutions, merely a more or less brown or red coloration is produced.

9. Solution of *mercuric chloride* added in excess to solutions of stannous chloride, or of stannous oxygen salts mixed with hydrochloric acid, produces a white precipitate of MERCUROUS CHLORIDE, owing to the stannous salt withdrawing half the chlorine from the mercuric chloride.

10. If a fluid containing a stannous salt and hydrochloric acid is added to a mixture of *potassium ferricyanide* and *ferric chloride*, a precipitate of PRUSSIAN BLUE separates immediately,

on account of the reduction of ferric ferricyanide to ferric ferrocyanide: $2Fe_2(Fe_2C_{12}N_{12}) + 4HCl + 2SnCl_2 = Fe_4(FeC_6N_6)_3 + H_4FeC_6N_6 + 2SnCl_4$. This reaction is extremely delicate, but it can be regarded as decisive only in cases where no other reducing agent is present.

11. From neutral or slightly acid solutions of stannous salts, *oxalic acid* precipitates a white, granular, quickly subsiding precipitate of STANNOUS OXALATE, SnC_2O_4 (difference from stannic salts). Concentrated solutions are precipitated immediately, but when more dilute, only after some time. Ammonium chloride prevents the precipitation. A solution of a stannous salt containing ammonium chloride and much oxalic acid is not precipitated by hydrogen sulphide.

12. From a solution of a stannous salt which is neutralized as far as possible with potassium hydroxide, *hydrogen peroxide*, upon warming, throws down all the tin as white, flocculent stannic hydroxide (W. FRENCH).

13. From solutions mixed with hydrochloric acid, *zinc* precipitates METALLIC TIN in the form of gray laminæ or of a spongy mass. If the experiment is made in a platinum capsule, the latter is not colored black (difference from antimony).

14. If stannous compounds mixed with *sodium carbonate* and some *borax*, or, better still, with a mixture of equal parts of *sodium carbonate* and *potassium cyanide*, or with *sodium formate*, are exposed on a charcoal support to the *inner blowpipe flame*, malleable grains of METALLIC TIN are obtained on cutting out and forcibly triturating the surrounding parts of charcoal with water in a small mortar, and washing off the charcoal from the metallic particles. Upon strongly heating the grains of metallic tin on a charcoal support, the latter becomes covered with a coating of white stannic oxide. The stick of charcoal (p. 34) is also admirably adapted for the reduction of tin.

15. If a trace of a stannous compound is added to a borax bead colored slightly blue by copper, and the bead is heated in the *lower reducing zone* of the non-luminous gas-lamp flame (p. 32), it will become reddish-brown to ruby-red, in consequence of the formation and separation of cuprous oxide

(compare § 140, 15). A compound of tin is essential to this reaction. The blowpipe flame cannot replace that of the gas-lamp, since in the former, cupric oxide can be reduced to cuprous oxide without the presence of tin.

16. Concerning the microchemical detection of stannous compounds, see HAUSHOFER, p. 153; BEHRENS, Zeitschr. f. analyt. Chem., **30**, 155; STRENG, Ber. d. deutsch. chem. Gesellsch., 1889, Ref., p. 34.

§ 153.

b. TIN, Sn, IN STANNIC COMPOUNDS. (*Stannic Oxide*, SnO_2.)

1. STANNIC OXIDE is a powder varying in color from white to straw-yellow, which upon heating transiently assumes a brown tint. When heated with concentrated sulphuric acid or fused with potassium disulphate, it gives compounds from which water separates all the stannic oxide. Other acids do not attack stannic oxide. When it is ignited with ammonium chloride, the tin volatilizes as stannic chloride. Stannic oxide forms with acids, bases, and water, two different series of compounds: the stannic oxide or stannic acid compounds, and the metastannic acid compounds. The chlorides (stannic chloride and metastannic chloride) correspond to the compounds with oxygen acids. The hydroxide precipitated from stannic chloride solution by alkalies dissolves easily in hydrochloric acid, but that produced by the action of nitric acid upon tin, metastannic hydroxide, does not dissolve in that acid. If the latter, however, is boiled a short time with hydrochloric acid, metastannic chloride, slightly soluble in hydrochloric acid, is formed, and if the excess of acid is now poured off and water is added, a solution of metastannic chloride, usually somewhat opalescent, results.

2. The STANNIC OXYGEN SALTS are colorless. The solutions of the normal salts redden litmus. The oxygen salts with volatile acids are easily decomposed by ignition. Anhydrous STANNIC CHLORIDE, $SnCl_4$, is a volatile liquid, strongly fuming in the air. It dissolves in cold water to stannic chloride solution. This is not precipitated by concen-

trated hydrochloric acid nor by sulphuric acid, unless it is *very* dilute, and it does not become yellow upon the addition of stannous chloride. The aqueous solution of metastannic chloride, on the other hand, is precipitated by concentrated hydrochloric acid and by sulphuric acid, and is colored yellow by stannous chloride. The dilute solutions of both chlorides are precipitated by boiling, and this takes place very rapidly with metastannic chloride.

3. By fusing stannic oxide, stannic hydroxide, or metastannic hydroxide with alkali-metal hydroxides, STANNATES soluble in water are formed, from the solutions of which, acids (even carbonic acid) separate stannic hydroxide. By fusing with alkaline carbonates, only a part of the stannic oxide is converted into stannate.

4. In stannic chloride solutions containing a moderate amount of free hydrochloric acid, *hydrogen sulphide* acting in excess produces a light yellow precipitate of STANNIC SULPHIDE, SnS_2, which contains stannic hydroxide, and does not change in color. In more dilute or less acid solutions, the precipitate is not always formed immediately, and it gradually becomes more intensely yellow. In very dilute solutions containing no free acid, the precipitate produced after some time is at first white, but afterwards yellow. Warming facilitates the precipitation. Alkaline solutions are not precipitated, and a great amount of free hydrochloric acid likewise prevents the precipitation. Oxalic acid, also, added in sufficient amount (35 to 40 parts of oxalic acid to 1 part of tin), prevents the precipitation (difference from antimony and arsenic, CLARKE, LESSER). The precipitate dissolves with some difficulty in ammonia, is nearly insoluble in ammonium carbonate, and insoluble in hydrogen potassium sulphite. It dissolves readily in potassium and sodium hydroxides, in alkaline sulphides, in concentrated, boiling hydrochloric acid, and also in aqua regia. The precipitate produced in metastannic chloride solutions by hydrogen sulphide, viz., stannic sulphide containing metastannic hydroxide, is formed slowly, especially in dilute solutions. It becomes more or less brown upon long standing under the liquid. An excess of sodium hydroxide dissolves the stannic sulphide out of it, leaving behind undissolved sodium

metastannate (BARFOED). Concentrated nitric acid converts all the precipitates produced by hydrogen sulphide into metastannic hydroxide. When ignited with a mixture of 5 parts of ammonium chloride and 1 part of ammonium nitrate, the precipitates behave in the same way as stannous sulphide (§ 152, 4). Upon deflagrating them with sodium nitrate and carbonate, sodium sulphate, stannic oxide, and some sodium stannate are obtained. If a solution of stannic sulphide in potassium hydroxide or sodium hydroxide is boiled with bismuth oxide or cupric oxide, sulphides of the latter metals are formed, while an alkaline stannate remains in solution.

5. *Ammonium sulphide* produces yellow, hydrous STANNIC SULPHIDE, which dissolves readily in an excess of the precipitant. From this solution, acids reprecipitate the stannic sulphide unaltered.

6. *Potassium* and *sodium hydroxides* give, in stannic chloride solutions, white precipitates of STANNIC HYDROXIDE, which dissolve readily in an excess of the precipitant. From metastannic chloride solutions, potassium hydroxide throws down METASTANNIC HYDROXIDE, which dissolves in a moderate excess of the precipitant. With a larger excess, potassium metastannate separates, which is difficultly soluble in potassium hydroxide, but soluble in water. From metastannic chloride solutions, sodium hydroxide precipitates white SODIUM METASTANNATE, which does not dissolve in an excess of sodium hydroxide. Stannic hydroxide as well as metastannic hydroxide, when dried over sulphuric acid, have a composition corresponding to the formula $SnO(OH)_2$.

7. *Potassium carbonate* gives a white precipitate in a stannic chloride solution. The precipitate, STANNIC HYDROXIDE, containing potassium, dissolves in an excess of the reagent, but separates again upon standing. The precipitate by *sodium carbonate* does not dissolve in an excess of the precipitant. The white precipitates which alkali-metal carbonates produce in metastannic chloride solutions dissolve scarcely or not at all in an excess of the precipitants.

8. *Sodium sulphate* or *ammonium nitrate* (in fact, most normal alkali-metal salts, when added in excess) throws down from both kinds of stannic solutions, *provided they are not too*

acid, the whole of the tin as STANNIC OR METASTANNIC HYDROXIDE. Heating promotes the precipitation: $SnCl_4 + 4Na_2SO_4 + 4H_2O = Sn(OH)_4 + 4NaCl + 4NaHSO_4$.

9. From solutions of stannic chloride, in the presence of free acid, *metallic zinc* precipitates METALLIC TIN in the shape of small, gray scales or as a spongy mass. If the operation is conducted in a platinum dish, no blackening of the latter is observed (difference from antimony).

10. If a stannic chloride solution is boiled for a long time with *metallic copper*, the stannic chloride is reduced to stannous chloride, and the solution then precipitates mercurous chloride from mercuric chloride solution (PATTISON MUIR).

11. Before the *blowpipe* or in the *gas flame*, the stannic compounds show the same reactions as the stannous compounds (compare § 152, 14 and 15). Stannic oxide is also readily reduced when fused with potassium cyanide in a glass tube or in a crucible.

12. In relation to the detection of stannic compounds by microchemical methods, see HAUSHOFER, p. 156; BEHRENS, Zeitschr. f. analyt. Chem., **30**, 155; STRENG, Ber. d. deutsch. chem. Gesellsch. 1889, Ref., p. 34.

§ 154.

c. ANTIMONY, Sb. (*Antimonious Oxide*, Sb_2O_3.)

1. METALLIC ANTIMONY has a bluish tin-white color, is lustrous, hard, brittle, fusible at 430°, and volatile at a very high temperature. When heated on charcoal before the blowpipe, it emits thick, white fumes of antimonious oxide, which form a coating on the charcoal. This combustion continues for some time, even after the removal of the metal from the flame; and is most distinctly visible if a strong current of air is thrown by the blowpipe directly upon the sample on the charcoal. But if the fumes ascend straight, the hot, metallic bead becomes surrounded with a net of brilliant, acicular crystals of antimonious oxide. Nitric acid oxidizes antimony readily. The dilute acid converts it almost entirely into antimonious oxide, while the more concentrated

the acid the more antimonic oxide (metantimonic acid) is formed, and the boiling, concentrated acid converts it almost completely into antimonic oxide. Neither of the two oxides is altogether insoluble in nitric acid; consequently, traces of antimony are always found in the acid fluid filtered from the precipitate. Even boiling hydrochloric acid, with exclusion of air, does not attack antimony. In nitro-hydrochloric acid, the metal dissolves readily, the solution containing antimonious chloride, $SbCl_3$, or antimonic chloride, $SbCl_5$, according to the degree of concentration of the acid and the duration of the action.

2. According to the mode of its preparation, ANTIMONIOUS OXIDE, Sb_2O_3, occurs in white and brilliant crystalline needles, or as a white powder. It fuses at a moderate red heat out of contact with air, and at a higher temperature, it volatilizes without decomposition. It is insoluble in water, almost insoluble in nitric acid, but dissolves readily in hydrochloric and tartaric acids. No separation of iodine takes place on boiling it with hydrochloric acid free from chlorine and potassium iodide free from iodic acid (BUNSEN). Antimonious oxide is easily reduced to metal by fusion with potassium cyanide.

3. ANTIMONIC OXIDE (or ACID), Sb_2O_5, is pale yellow. It forms three hydroxides with water: orthoantimonic acid, H_3SbO_4; pyroantimonic acid, $H_4Sb_2O_7$; and metantimonic acid, $HSbO_3$. These hydroxides are white, and they redden moist litmus-paper. The anhydrous acid and its hydrates scarcely dissolve in water, they are almost insoluble in nitric acid, but they dissolve rather readily in hot, concentrated hydrochloric acid, forming a solution containing antimonic chloride, $SbCl_5$, which becomes turbid upon the addition of water. On boiling antimonic acid with hydrochloric acid and potassium iodide, iodine separates, which dissolves in the hydriodic acid present to a brown fluid (BUNSEN). Upon ignition, antimonic acid loses oxygen, and is converted into infusible ANTIMONIOUS ANTIMONATE, Sb_2O_4. The potassium antimonates, pyroantimonates, and metantimonates are only partly soluble in water. Acids precipitate from the solutions the corresponding antimonic acids, and sodium chloride precipitates acid

sodium pyroantimonate from a solution of acid potassium pyroantimonate (§ 95, 2).

4. The ANTIMONIOUS SALTS of volatile oxygen acids are decomposed by ignition. The halogen salts are readily volatile without decomposition. The soluble, normal antimonious salts redden litmus-paper. With a large quantity of water, they are decomposed, with formation of insoluble basic salts and acid solutions containing antimony. Thus, *water*, when added in considerable amount, throws down from solutions of antimonious chloride in hydrochloric acid, a white, bulky precipitate of ANTIMONIOUS OXYCHLORIDE, $Sb_4O_5Cl_2$ (powder of Algaroth), which soon becomes heavy and crystalline. Tartaric acid dissolves this precipitate readily, and therefore prevents its formation if mixed with the solution previously to the addition of the water. It is this property that distinguishes this antimony compound from the basic bismuth salts formed under similar circumstances.

5. From acid solutions of antimonious salts (if the quantity of free mineral acid present is not too large), *hydrogen sulphide* precipitates the whole of the metal as orange-red, amorphous ANTIMONIOUS SULPHIDE, Sb_2S_3. In alkaline solutions, this reagent fails to produce a precipitate, or, at least, it precipitates them only imperfectly; and in neutral solutions, also, the metal is only partially thrown down by it. The antimonious sulphide produced is readily dissolved by potassium or sodium hydroxide and by alkali sulphides, especially if the latter contain an excess of sulphur. It is dissolved to a slight extent by ammonia, but if free from antimonic sulphide, it is almost insoluble in ammonium bicarbonate. It is insoluble in cold, dilute acids and in acid potassium sulphite. Concentrated hydrochloric acid of 1.18 sp. gr. dissolves it even in the cold, with evolution of hydogen sulphide, and, upon heating, it dissolves even in the acid of 1.12 sp. gr. Upon heating in the air, the precipitate gives a mixture of antimonious antimonate and antimony sulphide. If it is deflagrated with sodium nitrate, sodium sulphate and pyroantimonate are obtained. Ignited in a stream of chlorine or with a mixture of 5 parts of ammonium chloride and 1 part of ammonium nitrate, antimony sulphide is decomposed and

completely volatilized. If the latter operation takes place in a glass tube closed at one end, antimonious chloride is found in the sublimate. If the solution of antimonious sulphide in potassium hydroxide or potassium sulphide is boiled with bismuth oxide, bismuth sulphide is formed, and antimonious oxide remains dissolved in potassium hydroxide; and if the alkaline solution is boiled with cupric oxide, cuprous sulphide is produced, and the solution then contains potassium pyroantimonate. On fusing antimonious sulphide with potassium cyanide, metallic antimony and potassium sulphocyanide are formed. If the operation is conducted in a small tube expanded into a bulb at the lower end, or in a stream of carbon dioxide (see § 155, 13), no sublimate of antimony is produced. But if a mixture of antimonious sulphide with sodium carbonate or with potassium cyanide and sodium carbonate is heated in a glass tube in a stream of hydrogen gas (compare § 155, 4), a mirror of antimony is deposited in the tube, immediately beyond the spot occupied by the mixture.

From a solution of antimonic acid in hydrochloric acid, hydrogen sulphide throws down ANTIMONIC SULPHIDE, Sb_2S_5, mixed with antimonious sulphide and sulphur. The precipitate dissolves readily when heated with solution of caustic soda or ammonia, and easily in concentrated, boiling hydrochloric acid, with evolution of hydrogen sulphide and separation of sulphur, but it dissolves only very sparingly in a cold solution of hydrogen ammonium carbonate.

6. *Ammonium sulphide* produces in solutions of antimonious salts, an orange-red precipitate of ANTIMONIOUS SULPHIDE, which readily redissolves in an excess of the precipitant if the latter contains an excess of sulphur. Acids throw down from this solution antimonic sulphide, Sb_2S_5. However, in that case, the orange color usually appears of a lighter tint, owing to an admixture of sulphur.

7. If aqueous *sulphurous acid* is added to a solution of *sodium thiosulphate* (whereupon the solution becomes yellowish), and then some solution of an antimonious salt is also added, and the liquid is heated to boiling, it at first becomes turbid from the separation of sulphur, then the antimony separates as red ANTIMONY CINNABAR, Sb_2S_2O.

8. From solutions of antimonious chloride, and also of other simple antimonious salts—but far less completely, and mostly only after some time, from solutions of tartar emetic or analogous compounds—*potassium hydroxide*, *sodium hydroxide*, *ammonia*, *sodium carbonate*, and *ammonium carbonate* throw down a white, bulky precipitate of ANTIMONIOUS HYDROXIDE, which redissolves rather readily in an excess of potassium or sodium hydroxide, but requires the application of heat for its resolution in sodium carbonate, and is almost insoluble in ammonia.

9. From all solutions of antimonious salts, if they contain no free nitric acid, *metallic zinc* and likewise *metallic tin* (PIESZCZEK) precipitate METALLIC ANTIMONY as a black powder. If a few drops of a solution of antimony containing some free hydrochloric acid are put into a platinum capsule (the lid of a platinum crucible), and a fragment of zinc or tin is introduced, hydrogen containing hydrogen antimonide is evolved, and antimony separates, staining the part of the platinum covered by the liquid brown or black, even in the case of very dilute solutions. This reaction is to be highly recommended as equally delicate and characteristic. Cold hydrochloric acid of 1.12 sp. gr. soon removes the stain if it is very faint, but it removes it slowly and only upon warming if it is strong, while heating with nitric acid removes it immediately.

10. If the solution of an antimonious salt containing some hydrochloric acid is warmed with *bright iron*, *e.g.*, a piece of wire, all the antimony separates in a short time, with evolution of hydrogen, in the form of heavy, black flocks (difference from tin).

11. If a solution of antimonious oxide in potassium or sodium hydroxide is mixed with a solution of *silver nitrate*, a deep black precipitate, which was formerly believed to be argentous oxide, forms with the grayish-brown precipitate of argentic oxide. Upon now adding ammonia in excess, the latter is redissolved, while the black precipitate is left undissolved (H. ROSE). According to the investigations of PILLITZ, this is a variable mixture of antimony and silver, which may perhaps contain a chemical compound of both. This exceedingly delicate reaction affords an excellent means of detecting antimonious oxide in presence of antimonic acid.

12. If any solution of antimony in hydrochloric or sul-

phuric acid is introduced into a flask in which hydrogen gas is being evolved from pure *zinc* and dilute *sulphuric acid*, the zinc produces a reduction of the antimony compound in addition to the evolution of hydrogen. Antimony separates in the metallic state, but another portion of the metal combines with hydrogen, forming HYDROGEN ANTIMONIDE GAS, SbH_3. If this operation takes place in the apparatus which is used for MARSH'S test for arsenic (§ 155, 10), and after all the air has been expelled, the gas which is escaping from the fine opening is ignited,* the flame appears bluish-green from the antimony, separated by the decomposition of the hydrogen antimonide, burning in the flame. White fumes of antimonious oxide rise from it, which are readily deposited upon cold bodies and do not dissolve in water. However, if a cold body (a porcelain dish is best) is held in the flame, METALLIC ANTIMONY † is deposited upon it in an extremely fine state of division, forming a deep black and almost lusterless spot. If the middle part of the tube through which the gas is passing is heated to redness, the bluish-green tint of the flame decreases in intensity, and a metallic mirror of antimony of silvery luster is formed within the tube, on both sides of the heated part.

As compounds of arsenic give under the same circumstances similar stains or mirrors (§ 155, 10), it is always necessary to examine carefully the spots produced, in order to ascertain whether they really consist of antimony or contain any of that metal. With stains deposited on a porcelain dish, the object in view is most readily attained by treating them with a solution of sodium hypochlorite and sodium chloride (prepared by mixing a solution of calcium hypochlorite with sodium carbonate in some excess, and filtering), which will immediately dissolve arsenical stains, leaving those proceeding from antimony untouched, or at least removing them only after a very protracted action. A mirror within the glass tube, on the other hand, may be tested by heating it while the current of hydrogen gas still continues to pass through the tube. If the mirror volatilizes only at a rather high tem-

* The coloration of the flame appears especially distinct and pure when the gas escapes from a platinum jet.

† Whether this is actually antimony or perhaps solid hydrogen antimonide requires further investigation (J. W. RETGERS).

perature, and the hydrogen gas then issuing from the tube does not smell of garlic, and if it is only with a strong current that the ignited gas deposits spots on porcelain, and the mirror before volatilizing fuses to small, lustrous globules distinctly discernible through a magnifying glass, the presence of antimony may be considered certain. Moreover, the metals may be distinguished with great certainty by conducting through the tube a *very slow* stream of dry hydrogen sulphide, and heating the mirror moderately, proceeding in an opposite direction to that of the current. The antimonial mirror is by this means converted into antimonious sulphide, which appears of a more or less reddish-yellow color, but looks black if it becomes crystalline. If a feeble stream of dry hydrochloric acid gas is now transmitted through the glass tube, the antimonious sulphide, if present in thin layers only, disappears immediately; while if the incrustation is somewhat thicker, it takes a short time to dissipate it. The reason for this is that the antimonious sulphide decomposes readily with hydrochloric acid, and the antimonious chloride formed is exceedingly volatile in a stream of hydrochloric acid gas. If the gaseous current is now conducted into some water, the presence of antimony in the latter fluid may be readily proved by means of hydrogen sulphide. By this combination of reactions, antimony may be distinguished with positive certainty from all other metals. The reactions which hydrogen gas containing hydrogen antimonide shows with solutions of silver nitrate and mercuric chloride, and with solid potassium hydroxide, will be found in § 157, 7.

13. If a solution of antimonious oxide in *potassium* or *sodium hydroxide* is heated with *aluminium* or with *zinc* and a little *magnesium*, all the antimony separates, and hydrogen is evolved. Hydrogen antimonide does not go off in this case (difference from arsenious acid, which gives hydrogen arsenide when subjected to this treatment, HAGER, GATEHOUSE).

14. If a mixture of a compound of antimony with *sodium carbonate* and *potassium cyanide* or with *sodium formate* is exposed on a charcoal support to the *reducing flame of the blowpipe*, brittle globules of METALLIC ANTIMONY are produced, which may be readily recognized by the peculiar reactions that mark their oxidation (compare § 154, 1).

15. In the upper reducing flame of the gas-lamp (p. 32), compounds of antimony give a greenish-gray color, and no odor. The *metallic incrustation* is black, sometimes dull, sometimes bright. The *incrustation of oxide* is white. When moistened with entirely neutral silver nitrate and then blown on with ammonia, it gives a black spot (BUNSEN).

16. In relation to the microchemical detection of antimony, see HAUSHOFER, p. 14; BEHRENS, Zeitschr. f. analyt. Chem., **30**, 163.

§ 155.

d. ARSENIC, As, and ARSENIOUS COMPOUNDS.

(*Arsenious Oxide or Acid*, As_2O_3.)

1. METALLIC ARSENIC, in a microcrystalline condition, is black (J. W. RETGERS), but when it is in distinct crystals, it is steel-gray, and has a high luster, which it retains in dry air, but loses in moist air by becoming superficially oxidized. The metallic arsenic of commerce is therefore commonly dull, with a dim, bronze luster on the planes of crystallization. Arsenic is not very hard, but very brittle, and at a dull red heat, under ordinary pressure, it volatilizes without fusion. The fumes escaping into the air have a most characteristic odor of garlic, which is ascribed to a suboxide of arsenic occurring in a state of vapor. Heated with free access of air, arsenic burns—at an intense heat, with a bluish flame—emitting white fumes of arsenious oxide, which condense on cold bodies. If arsenic is heated in a glass tube sealed at the lower end, the greater part of it volatilizes unoxidized; and if it is heated in a stream of carbonic acid, it volatilizes wholly unoxidized, and recondenses above or beyond the heated spot as a sublimate (arsenical mirror). This is usually brilliantly gray next to the heated part (crystalline), and beyond this it is black (microcrystalline). Upon heating in a stream of hydrogen, in addition to the arsenic mirror, a more volatile, brown sublimate of solid hydrogen arsenide is formed (RETGERS). In contact with air and water, arsenic oxidizes slowly to arsenious acid. Weak nitric acid converts it, with the aid of heat,

into arsenious oxide, which dissolves only sparingly in an excess of the acid; but strong nitric acid converts it partially into arsenic acid. It is insoluble in hydrochloric acid and dilute sulphuric acid, while concentrated, boiling sulphuric acid oxidizes it to arsenious oxide, with evolution of sulphur dioxide. It dissolves in aqua regia easily to arsenic acid.

2. ARSENIOUS OXIDE or ACID, in the amorphous condition, is a colorless, transparent, glassy mass. In the crystalline condition, it forms a white, porcelain-like mass or occurs also in well-formed crystals. When pulverized, it appears as a heavy, white, gritty powder. When heated, it volatilizes in white, inodorous fumes. If the operation is conducted in a glass tube, a sublimate is obtained, consisting of small, brilliant octahedrons and tetrahedrons. Arsenious acid is only difficultly moistened by water, and comports itself in this respect like a fatty substance. It is sparingly soluble in cold, but more readily in hot water. It is copiously dissolved by hydrochloric acid, as well as by solutions of potassium and sodium hydroxides. Upon boiling with nitro-hydrochloric acid, it dissolves to arsenic acid. It is highly poisonous.

If a small fragment of arsenious oxide is placed in the point of a drawn-out glass tube (Fig. 36), and a *splinter of charcoal*, broken from a piece that has been freshly ignited,

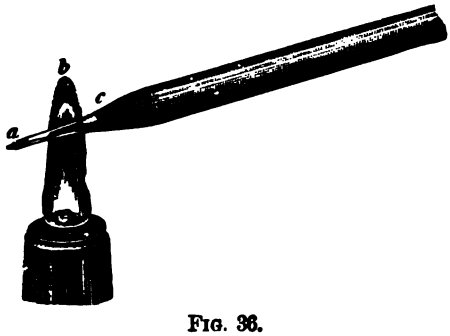

FIG. 36.

is placed above it, and the latter is first heated to redness and then the arsenious oxide is also heated, the vapors of the arsenious oxide are reduced by the red-hot charcoal, and a MIRROR OF METALLIC ARSENIC is obtained. If the tube

is now cut off between *a* and *c*, and is heated in an inclined position (with *c* at the top), the arsenic is volatilized, giving the garlic-like odor. This is the simplest as well as the surest method of detecting pure arsenious acid.

3. The ARSENITES are mostly decomposed upon ignition, either into arsenates and metallic arsenic which volatilizes, or into arsenious oxide and the base with which it was combined. Of the arsenites, only those with alkali bases are soluble in water. The insoluble arsenites are dissolved, or at least decomposed, by hydrochloric acid. Anhydrous ARSENIOUS CHLORIDE, $AsCl_3$, is a colorless volatile liquid, fuming in the air, which will bear the addition of a little water, but is decomposed by a larger amount into arsenious oxide, which partly separates, and hydrochloric acid, which retains the rest of the arsenious oxide in solution. If a solution of arsenious oxide in hydrochloric acid is evaporated by heat, arsenious chloride escapes along with the hydrochloric acid. When such a solution is heated in a distilling apparatus, the arsenic is obtained in the form of arsenious acid in the distillate, which also contains hydrochloric acid. If the distillation is repeated with renewed additions of fuming hydrochloric acid, all the arsenious acid is obtained in the distillate.

4. *Hydrogen sulphide* colors aqueous solutions of arsenious acid yellow, but produces no precipitate in them. It fails equally to give a precipitate in aqueous solutions of normal alkali arsenites, but upon addition of a strong acid, a bright yellow precipitate of ARSENIOUS SULPHIDE, As_2S_3, forms at once. The same compound forms in like manner in the hydrochloric acid solution of arsenites insoluble in water. Even a large excess of concentrated hydrochloric acid does not prevent complete precipitation. Alkaline solutions are not precipitated. Arsenious sulphide is readily and completely dissolved by alkalies, normal alkali carbonates, and also by alkali sulphides. Freshly precipitated arsenious sulphide is also soluble in alkali-metal acid sulphites. It is nearly insoluble in hydrochloric acid, even though concentrated and boiling. Boiling nitric acid decomposes and dissolves the sulphide readily.

The deflagration of arsenious sulphide with sodium car-

bonate and nitrate gives rise to the formation of sodium arsenate and sulphate. When it is heated with a mixture of 5 parts of ammonium chloride and 1 part of ammonium nitrate, in a glass tube, complete volatilization takes place. The arsenic is found in the sublimate as arsenious chloride. When a solution of arsenious sulphide in ammonia is heated with an excess of hydrogen peroxide, a clear liquid is produced, containing ammonium sulphate and arsenate. Upon boiling a solution of arsenious sulphide in sodium sulphide, or, also, in potassium or sodium hydroxide, with bismuth hydroxide, carbonate, or basic nitrate, bismuth sulphide and potassium (or sodium) arsenite are produced. By boiling such a solution with cupric oxide, cuprous sulphide and sodium (or potassium) arsenate are formed.

If arsenious sulphide is mixed with 3 or 4 parts of sodium carbonate, with the addition of a little water, the pasty mass is then spread out upon small fragments of glass, and after this has been well dried, it is quickly heated to redness in a glass tube through which dry hydrogen is being passed, the greater part of the arsenic will be reduced and driven off if the temperature is high enough. A part of that which is driven off is obtained as a metallic mirror in the tube, and the more volatile, brown sublimate of solid hydrogen arsenide is likewise formed. The rest of the arsenic escapes as gaseous hydrogen arsenide with the hydrogen, and when the latter is ignited, it gives a bluish color to the flame, and, when a porcelain dish is held in the latter, causes the production of brownish-black stains of solid hydrogen arsenide (RETGERS). This method of reduction gives accurate results, but does not permit the distinction of arsenic from antimony with sufficient certainty, or the detection of the former in the presence of the latter (compare § 154, 5), and the method is therefore generally replaced by the reducing operation described in § 155, 13.

5. *Ammonium sulphide* also causes the formation of ARSENIOUS SULPHIDE. In neutral and alkaline solutions, however, the arsenious sulphide does not precipitate, but remains dissolved as ammonium sulpharsenite, yet from this solution, it precipitates immediately upon the addition of a free acid.

6. *Silver nitrate*, added in slight excess, leaves aqueous solutions of arsenious acid perfectly clear, or at least produces only a trifling yellowish-white turbidity in them; but if a little ammonia is added, a yellow precipitate of SILVER ARSENITE, Ag_3AsO_3, separates. Upon the addition of silver nitrate to the solution of a normal alkali-metal arsenite, an almost white precipitate is formed, which becomes yellow only upon the addition of a little potassium hydroxide. Silver arsenite dissolves readily in nitric acid as well as in ammonia when some alkaline nitrate is present, and is not insoluble in ammonium nitrate. If, therefore, a small quantity of the precipitate is dissolved in a large amount of nitric acid, and the latter is afterwards neutralized with ammonia, the precipitate does not make its appearance again, since it remains dissolved in the ammonium nitrate formed. The reaction is produced most delicately by adding a layer of ammonia upon the top of the liquid to which silver nitrate has been added. The precipitate then appears at the point of contact of the two liquids as a yellowish zone. If a solution of arsenious acid is heated to boiling after the addition of a small excess of silver nitrate and a moderate excess of ammonia, METALLIC SILVER separates, while the arsenious acid is converted into arsenic acid.

7. *Cupric sulphate* does not produce a precipitate in aqueous solutions of arsenious acid, but upon the addition of an alkali, a yellowish-green precipitate of CUPRIC ARSENITE, $CuHAsO_3$, is produced. This dissolves in potassium hydroxide as well as in sodium hydroxide to a blue liquid, from which cuprous oxide separates upon boiling (compare 8).

8. If arsenious acid is dissolved in an excess of potassium or sodium hydroxide, or if potassium or sodium hydroxide is added in excess to the solution of an alkaline arsenite, and a small amount of a very dilute solution of *cupric sulphate* is then added, a clear, blue solution is obtained, which upon boiling gives a red precipitate of CUPROUS OXIDE. The solution contains potassium or sodium arsenate. This reaction succeeds easily, and is exceedingly delicate provided not too much of the cupric sulphate is used. Even should the red precipitate be so exceedingly minute as to escape detection when looking across the tube, yet it will always be discernible with great distinctness upon looking down the test-tube.

Although this reaction is really of great importance in certain instances as a confirmatory proof of the presence of arsenious acid, and more particularly, also, as a means of distinguishing that acid from arsenic acid, yet it is entirely inapplicable for the direct detection of arsenic, since grape-sugar and other organic substances produce cuprous oxide from cupric salts in the same manner.

9. If a solution of arsenious oxide mixed with hydrochloric acid is heated with a perfectly clean strip of *copper* or copper wire, an iron-gray, metallic film is deposited on the copper,

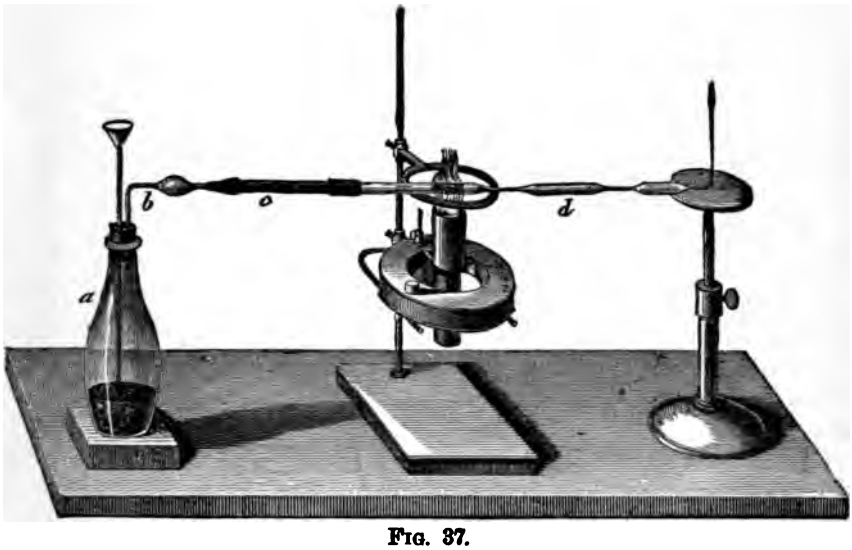

FIG. 37.

even in highly dilute solutions; and when this film increases in thickness, it peels off in black scales. If after washing off the free acid, the coated copper is heated with solution of ammonia, the film peels off from the copper, and separates in the form of minute spangles (REINSCH). These are not pure arsenic, but consist of COPPER ARSENIDE, Cu_3As_2. If the substance, either simply dried or oxidized by ignition in a current of air (which is attended with escape of some arsenious acid), is heated in a current of hydrogen, there escapes relatively but little arsenic, alloys richer in copper being left behind (FRESENIUS, LIPPERT). Only after the presence of arsenic in the alloy has been fully demonstrated, can this reac-

tion be considered a decisive proof of the presence of that metal, as under the same circumstances, antimony and other metals will also precipitate in a similar manner upon copper, and a black coating is formed upon the copper in the presence of sulphurous acid.

10. If an acid or neutral solution of arsenious acid or any of its compounds is mixed with *zinc*, *water*, and *dilute sulphuric acid* or *hydrochloric acid*, HYDROGEN ARSENIDE, AsH_3, is formed, in the same manner that compounds of antimony give hydrogen antimonide under analogous circumstances (compare § 154, 12). This reaction affords a means for the detection of even the most minute quantities of arsenic. The operation is conducted in the apparatus illustrated in Fig. 37, or in one of similar construction.* *a* is the evolution-flask; *b*, a bulb intended to receive the water carried with the gaseous current; *c*, a tube filled with cotton wool and small lumps of calcium chloride for drying the gas.† This tube is connected with *b* and *d* by rubber tubes which have been boiled in a solution of sodium hydroxide; *d* should have an inner diameter of 7 mm (Fig. 38), and must be made of difficultly fusible glass, free from lead and as free as possible from arsenic. In experiments requiring great accuracy, the tube should be drawn out as shown in Fig. 37. Not too small a quantity of zinc, as pure as possible, but in any case entirely free from arsenic,‡ is placed in the evolution-flask, water is poured through the funnel-tube until the end of it is covered, and then pure sulphuric acid diluted with 3 parts of water is added gradually through the funnel-tube, so that a uniform and moderate stream of hydrogen is produced. As soon as it is certain

FIG. 38.

* I prefer the very convenient form of MARSH'S apparatus, which is recommended by F. J. OTTO.

† A bulb-tube containing a little concentrated sulphuric acid may also be used for drying the gas (LYTTKENS, LENZ).

‡ Since zinc which is entirely free from other metals evolves hydrogen with dilute sulphuric acid only very slowly, it was formerly customary to add a trace of platinic chloride to the liquid, which causes a lively evolution of hydrogen to take place at once. But since, according to THIELE, the delicacy of the arsenic reaction is thus diminished, it is more advisable to use zinc containing a trace of iron, such as is obtained when molten zinc is stirred with an iron rod (L. L'HÔTE).

that all the air has been driven out of the apparatus, the gas escaping from the tube *d* is ignited. It is advisable to wrap a towel around the flask before kindling the gas, to guard against accidents in case of an explosion. It is first absolutely necessary to ascertain whether the zinc and the sulphuric acid are quite free from any admixture of arsenic. This is done by depressing a porcelain dish horizontally upon the flame, in order to make it spread over the surface; and if the hydrogen contains hydrogen arsenide, brownish or brownish-black stains of solid hydrogen arsenide will appear on the porcelain. If this is not the case, in addition to the above test, in accurate experiments, the part of the tube *d* shown in the figure is heated to redness for some time, to see whether the arsenic coating does not show itself at the narrowed part of the tube. When it is certain that the hydrogen is pure, the liquid to be tested for arsenic is poured through the funnel-tube, and the latter is rinsed with water. It is to be *emphatically* recommended that only a very little of the liquid to be tested should be put in at first, since in cases where the quantity of arsenic present is considerable, and a somewhat large supply of the fluid is poured into the flask, the evolution of gas often proceeds with such violence as to stop the further progress of the experiment.

Now if the fluid which is added contains an oxygen or halogen compound of arsenic, there is immediately evolved, along with the hydrogen, the exceedingly poisonous hydrogen arsenide, which at once imparts a bluish tint to the previously colorless flame of the kindled gas. At the same time, white fumes of arsenious acid arise, which condense upon cold objects. If a porcelain dish is now depressed upon the flame, solid hydrogen arsenide condenses upon the dish in black stains in a manner similar to antimony (see § 154, 12). The stains formed by arsenic, however, incline more to a blackish-brown tint, and show a bright luster; while the antimonial stains are dull and of a deep black color. The arsenical stains may be distinguished, moreover, from those of antimony by solution of sodium hypochlorite with sodium chloride (compare § 154, 12), which will at once dissolve arsenical stains, leaving antimonial stains unaffected, or removing them only after a considerable time. The stains may also be recog-

nized as those of arsenic by warming them with a few drops of concentrated nitric acid. They dissolve to arsenic acid, which may then be easily detected with ammonium molybdate (see § 156, 9, DENIGÈS).

If the tube *d* is strongly heated at the place indicated in the figure, a brilliant arsenical mirror makes its appearance in front of or in the narrowed portion of the tube, beyond the heated part. This mirror is of a darker and less silvery-white hue than that produced by antimony under similar circumstances. It is distinguished, moreover, from the latter by the facility with which it may be driven forward in a current of hydrogen gas without previous fusion, and also by the characteristic odor of garlic emitted by the escaping (unkindled) gas. If the gas is kindled while the mirror in the tube is being heated, the flame, even with a very slight current of gas, will deposit arsenical stains on a porcelain plate.

The reactions and properties just described are amply sufficient to enable us to distinguish between arsenical and antimonial stains and mirrors; but they will often fail to detect arsenic, with positive certainty, in presence of antimony. In cases of this kind, the following process will serve to set at rest all possible doubt as to the presence or absence of arsenic: Heat to redness in several places the long tube through which the gas to be tested is passing, in order to produce metallic mirrors which are as strong as possible; then transmit through the tube a very slow stream of dry hydrogen sulphide, and heat the metallic mirrors with a gas- or simple alcohol-lamp, proceeding in a direction opposite to that of the current of gas. If arsenic alone is present, yellow arsenious sulphide is formed inside the tube; if antimony alone is present, an orange-red or black antimonious sulphide is produced; and if the mirror consisted of both metals, the two sulphides appear side by side, the arsenious sulphide, as the more volatile, lying invariably beyond the antimonious sulphide. If dry hydrogen chloride gas is now transmitted through the tube containing either sulphide or both sulphides, without applying heat, no alteration will take place if arsenious sulphide alone is present, even though the gas be passed through the tube for a considerable time. If antimonious sulphide alone is present,

this will entirely disappear, as already stated (see § 154, 12); and if both sulphides are present, the antimonious sulphide will immediately volatilize, while the yellow arsenious sulphide will remain. If a small quantity of ammonia solution is now drawn into the tube, the arsenious sulphide dissolves, and thus may be readily distinguished from sulphur which may have separated. Personal experience has convinced me of the infallibility of these combined tests for the detection of arsenic. The following method of distinguishing stains depends upon the same chemical processes: The stains are obtained upon a glass plate, they are moistened with ammonium sulphide, this is allowed to evaporate by the aid of heat, then the glass plate is placed, with the stains turned downward, upon a beaker containing a little fuming hydrochloric acid. If antimony only is present, the orange-colored residue disappears, while in presence of arsenic, yellow arsenious sulphide remains behind (J. T. ANDERSON).

The reaction of hydrogen containing hydrogen arsenide with solution of silver nitrate and of mercuric chloride will be found in § 157, 7.

MARSH was the first to suggest the method of detecting arsenic by the production of hydrogen arsenide.

11. If a few drops of *stannous chloride* solution are added to about 5 cc of fuming hydrochloric acid, and a few drops of a solution of arsenious acid or of an arsenite are added, the arsenious acid is reduced, and a brownish-black precipitate is obtained (BETTENDORF).* The reaction, which takes place slowly in the cold, but rapidly by heating, is very delicate, and occurs only in the presence of an excess of fuming hydrochloric acid. If the hydrochloric acid has a lower specific gravity than 1.123, the precipitation is incomplete, or does not occur at all. If one has occasion to make frequent tests for arsenic by this method, it is convenient to keep on hand a solution of stannous chloride in extremely concentrated hydrochloric acid (38 per cent). Antimonious acid is not reduced under the same conditions.

* Whether the precipitate is arsenic or solid hydrogen arsenide requires further investigation (RETGERS).

12. If to a solution of arsenious acid or of an arsenite an equal or double amount of concentrated hydrochloric acid and a little *sodium hypophosphite* are added, and it is heated to boiling, a brownish-black precipitate like that mentioned in 11 separates, if the quantity of arsenic is not very small. With very small amounts of arsenic, only a yellowish-brown to brown coloration of the liquid results, even after long heating. The addition of a crystal of potassium iodide considerably heightens the delicacy of the reaction, but this cannot be used in the presence of such substances as give precipitates with potassium iodide or which separate iodine from it (LOOF, THIELE).

13. If arsenites, arsenious acid, or arsenious sulphide are fused with a mixture of 3 parts of dry *sodium carbonate* and 1 part of *potassium cyanide*, all the arsenic is reduced, and certain bases present at the same time may also be reduced, the oxygen converting a part of the potassium cyanide into cyanate. In the reduction of arsenious sulphide, potassium sulphocyanide is formed. While all the arsenic is volatilized upon the reduction of arsenious acid and arsenious sulphide, and is obtained as a mirror if the reduction is carried out in an appropriate apparatus, still mirrors are obtained from arsenites only when their bases are not reduced to arsenides at all, or are reduced to such arsenides as lose their arsenic wholly or partly by heating. This method of reducing arsenic compounds with potassium cyanide deserves special attention on account of its simplicity, the certainty of its results even in the presence of very small amounts of arsenic, and because of the neatness with which it can be performed. It is excellently adapted for the direct production of metallic arsenic from arsenic sulphide, in which respect it undoubtedly excels all other methods in simplicity and accuracy. Formerly, when glass tubes were free from arsenic, the experiment could be made with complete safety in a glass tube blown into a small bulb at the lower end, or better, with the use of a slow stream of carbonic acid, directly in a glass tube drawn out to a long point. Now, however, since nearly all the glass tubes of commerce contain

arsenic,* the reduction must take place in such a manner that the fusing mixture of potassium cyanide and sodium carbonate does not come in contact with the glass. The apparatus described by myself and L. v. BABO, therefore, requires a slight modification of the form in which it was described in previous editions, and is given that shown in Fig. 39.

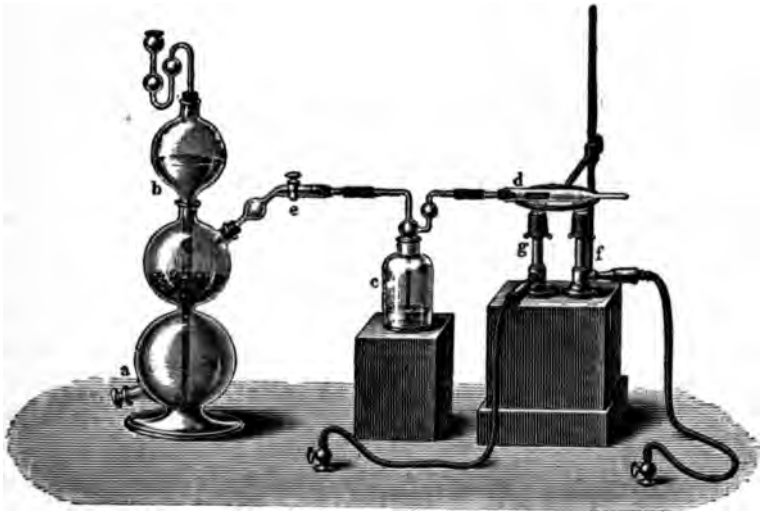

FIG. 39.

a b is a KIPP'S apparatus charged with pieces of marble and pure, dilute hydrochloric acid, for the evolution of carbonic acid;† *c* is a wash-bottle which contains some pure, concentrated sulphuric acid for the purpose of drying the car-

FIG. 40.

bonic acid; *d* is a tube of difficultly fusible glass, free from lead, which is made over the blast-lamp from a piece of

*Compare W. FRESENIUS, "Der Arsengehalt des Glases als eine Fehlerquelle bei der Nachweisung von Arsen." Zeitschr. f. analyt. Chem., 22, 397.

† Instead of this, any other carbonic acid generator with which the stream of gas may be accurately regulated by means of a stop-cock will, of course, serve the purpose.

tubing like that used for the elementary analysis of organic substances. This is shown in Fig. 40, one half natural size. The tube must be large enough so that the porcelain boat (shown in Fig. 41, natural size) used for the purpose of heating the mixture may be pushed into it.

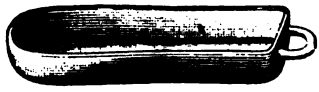

Fig. 41.

When the apparatus is set up, and filled with carbonic acid, the completely dry arsenious sulphide or other arsenious salt which is to be reduced is triturated in a slightly warmed mortar with 12 parts of a completely arsenic-free, well-dried mixture (§§ 49 and 57), consisting of 3 parts of sodium carbonate and 1 part of potassium cyanide. The powder is transferred to the porcelain boat and is introduced into the reduction-tube in the position shown in Fig. 39. The tube is then connected with the wash-bottle, a moderate stream of carbonic acid is allowed to escape by opening the stop-cock *e* (Fig. 39), and the mixture is dried in the most careful manner by gently warming the boat and also the tube throughout its whole length, by means of a flame. When every particle of deposited water has disappeared from the tube, the stream of carbonic acid is moderated so that single bubbles go through the sulphuric acid at intervals of about one second. The end of the thick part of the tube, where it begins to narrow, is now heated to redness by means of the lamp *f*. When this temperature has been reached, the boat is heated by the lamp *g*, at first moderately so that the fusing mass does not spatter, afterwards strongly and persistently until all the arsenic is driven out. If any of the latter should have deposited in the wider part of the tube, this is also heated, progressing towards the drawn-out end. The whole amount of the reduced arsenic is then found as a metallic mirror (Fig. 42) beyond the part of the tube

Fig. 42.

heated to redness by the burner *f*, which is kept in place during the whole operation. A small part of the arsenic escapes from the point of the tube, and imparts to the air a

garlic-like odor. The point of the tube may be finally closed by fusion, and the mirror may be driven together towards the thicker part by carefully heating the small end of the tube, by which means, it assumes an especially fine and pure metallic appearance. In this manner, even $\frac{1}{100}$ of a milligram of arsenious acid gives a recognizable arsenic mirror.* Antimony sulphide and other antimony compounds give no metallic mirror when treated in this way.

14. If arsenious oxide or an arsenite is exposed on charcoal to the *reducing flame of the blowpipe*, the frequently mentioned, highly characteristic odor resembling garlic is emitted, more especially if some sodium carbonate is added. This odor has its origin in the reduction and reoxidation of the arsenic, and enables us to detect very minute quantities. This test, however, like all others that are based upon the indications of the sense of smell, cannot be implicitly relied on.

15. Concerning the detection of arsenic in the microchemical way, see HAUSHOFER, p. 15; BEHRENS, Zeitschr. f. analyt. Chem., **30**, 164; EMICH, *ibid.*, **32**, 167.

§ 156.

e. ARSENIC COMPOUNDS. (*Arsenic Acid*, As_2O_5.)

1. ARSENIC ACID free from water (arsenic anhydride) forms a colorless or white, glassy, fusible mass, which dissolves slowly in cold water, more rapidly in hot water, and decomposes into oxygen and arsenious acid at a strong red heat. ARSENIC HYDROXIDE (orthoarsenic acid) containing water of crystallization, $2H_3AsO_4.H_2O$, is deposited from the solutions at a low temperature, in the form of perfectly colorless and transparent, prismatic crystals, which deliquesce in moist air and lose their water at 100°. At 180°, PYROARSENIC ACID, $H_4As_2O_7$, is obtained; at 206°, METARSENIC ACID, $HAsO_3$, is formed; and at a temperature near redness, the anhydride

*Compare W. FRESENIUS, "Ueber die richtige Ausführung und der Empfindlichkeit der FRESENIUS-BABO'schen Methode zur Nachweisung des Arsens." Zeitschr. f. analyt. Chem., **20**, 531.

is left. All the acids dissolve in water to orthoarsenic acid. Arsenic acid acts as a poison.

2. The arsenates correspond in composition to the acids, and it is therefore customary to distinguish orthoarsenates, pyroarsenates, and metarsenates. The orthoarsenates, corresponding to the orthophosphates, are (according to the old nomenclature) either basic, neutral, or acid salts, respectively, as they contain 3 equivalents of the base and no hydroxyl, 2 equivalents of the base and 1 equivalent of hydroxyl, or 1 equivalent of the base and 2 equivalents of hydroxyl. The salts of the alkali metals and the acid salts of the alkali-earth metals are soluble in water, while almost all the other arsenates dissolve in hydrochloric or nitric acid. The anhydrous arsenates of fixed bases are not decomposed by heat.

A solution of arsenic acid or of an arsenate in hydrochloric acid may be boiled for a long time without losing arsenious chloride by volatilization, if it does not contain too much hydrochloric acid. It is only when the residue consists of about equal parts of hydrochloric acid of 1.12 sp. gr. and water that traces of arsenious chloride escape with the hydrochloric acid. If, on the other hand, arsenic acid is heated with concentrated hydrochloric acid, some arsenious chloride and chlorine escape. If arsenic acid is distilled repeatedly with concentrated hydrochloric acid and ferrous chloride, all the arsenic is volatilized as arsenious chloride and obtained in the distillate.

3. *Hydrogen sulphide* fails to precipitate alkaline and neutral solutions, and in moderately acid solutions, it occasions no precipitate at first *in the cold*. Upon long standing, a partial reduction of arsenic acid to arsenious acid takes place, accompanied by the separation of colloidal arsenic sulphide, As_2S_4, and sulphur; then there is a precipitation of yellow ARSENIC SULPHIDE and ARSENIOUS SULPHIDE. This process continues until all the arsenic is finally precipitated (BRAUNER and TOMICEK, THIELE). From solutions which contain at least 2 parts of concentrated hydrochloric acid of 1.2 sp. gr. to 1 part of water, hydrogen sulphide precipitates ARSENIC SULPHIDE very quickly (FR. NEHER.)

If hydrogen sulphide is conducted into a moderately acid solution of arsenic acid, which is *warmed to about* 70°, ARSENIC

SULPHIDE, As_2S_3, is also obtained if hydrogen sulphide is largely in excess (BUNSEN), but otherwise the precipitate consists of a mixture of arsenic sulphide, arsenious sulphide, and sulphur. If sulphurous acid, or sodium sulphite with hydrochloric acid, is added to a solution of free arsenic acid or of an arsenate, the sulphurous acid reacts with the arsenic acid (most quickly by heating), and arsenious acid and sulphuric acid are formed. If hydrogen sulphide is now added, the whole of the arsenic is immediately precipitated as ARSENIOUS SULPHIDE.

4. In neutral and alkaline solutions, *ammonium sulphide* changes arsenic acid into arsenic sulphide, which remains in solution as ammonium sulpharsenate. This compound is decomposed by the addition of an acid, and arsenic sulphide separates. The separation takes place more quickly than that by hydrogen sulphide from cold, moderately acid solutions. It is facilitated by warming. The precipitate is not a mixture of arsenious sulphide and sulphur, but is ARSENIC SULPHIDE.

5. In solutions of arsenic acid and of alkali-metal arsenates, *silver nitrate* produces a very characteristic, reddish-brown precipitate of SILVER ARSENATE, Ag_3AsO_4, which is readily soluble in dilute nitric acid and in ammonia, and dissolves also slightly in ammonium nitrate. Accordingly, if the precipitate is dissolved in some nitric acid, and a layer of dilute ammonia is brought above the solution, a precipitate is produced at the surface of contact of the two liquids and forms a ring. The addition of some sodium acetate increases the delicacy of the reaction. If, however, but little of the precipitate is dissolved in very much nitric acid, the precipitate often does not form again upon neutralizing with ammonia, on account of the solvent action of ammonium nitrate. The ammoniacal solution of silver arsenate does not deposit silver upon boiling (difference between arsenic and arsenious acids).

6. *Cupric sulphate* does not produce a precipitate in aqueous solutions of arsenic acid. Upon the addition of an alkali, a bluish-green precipitate of COPPER ARSENATE is formed. Upon the addition of more potassium or sodium hydroxide, the color changes to a beautiful, light blue, while the precipitate does not dissolve. Upon boiling, no cuprous oxide is formed (difference between arsenic and arsenious acids).

7. If a dilute solution of arsenic acid mixed with some hydrochloric acid is heated with a clean strip of *copper*, the metal remains perfectly bright (WERTHER, REINSCH); but if to 1 volume of the solution 2 volumes of concentrated hydrochloric acid are added, a gray film is deposited on the copper, as in the case of arsenious acid. Under these circumstances, the reaction is just as delicate as with arsenious acid (REINSCH).

8. If a solution of arsenic acid, or of an arsenate soluble in water, is added to a clear mixture of *magnesium sulphate, ammonium chloride*, and not too little *ammonia*, a crystalline precipitate of AMMONIUM MAGNESIUM ARSENATE, $NH_4MgAsO_4.6H_2O$, separates—from concentrated solutions immediately, from dilute solutions after some time. If a small portion of the precipitate is dissolved on a watch-glass in a drop of nitric acid, a little silver nitrate added, and the solution touched with a glass rod dipped in ammonia, brownish-red silver arsenate is formed. Or, if a small portion of the precipitate is dissolved in hydrochloric acid, and hydrogen sulphide is passed into the solution with warming, a yellow precipitate is formed. (Differences between ammonium magnesium arsenate and phosphate.)

9. If a small amount of a solution of arsenic acid or of an arsenate is added to a few cubic centimeters of the solution of *ammonium molybdate* in nitric acid, no precipitate is formed in the cold, even after long standing. Upon heating, however, a bright yellow precipitate of AMMONIUM ARSENO-MOLYBDATE separates, which under the microscope is shown to consist of needles grouped in star-shaped forms. The precipitate is soluble in ammonia. In the colorless solution thus obtained, the magnesia mixture mentioned in 8 produces the reaction there described.

10. Arsenic compounds deport themselves in the same way as those of arsenious acid, with *stannous chloride*, with *sodium hypophosphite and hydrochloric acid*, with *zinc* in the presence of sulphuric acid, with *potassium cyanide*, and before the *blowpipe*. If the reduction of arsenic acid is effected by means of zinc in a platinum dish, the platinum is not colored black (difference from antimony).

11. In relation to the detection of arsenic in the micro-

chemical way, see HAUSHOFER, p. 15; BEHRENS, Zeitschr. f. analyt. Chem., **30**, 164.

§ 157.

Recapitulation and Remarks.—Various methods may be used for the detection of the metals of the second division of the sixth group, in mixtures or solutions containing all or several of them, and it is not possible to decide at once which process is the best. On the contrary, sometimes one method and sometimes another deserves preference, according to the relative amounts of the metals present, and whether it is a question of the greatest possible convenience or of rapidly attaining the end without demanding the highest degree of exactness.

The different ways of effecting the detection or separation of tin, antimony, and arsenic, when present together, will be described first, and afterwards the means of distinguishing between the several oxides and acids of the three metals, and also the methods of separating gold and platinum from tin, antimony, and arsenic.

1. If a dry mixture of sulphides of tin, antimony, and arsenic is to be examined, triturate 1 part of it with 1 part of dry sodium carbonate and 1 part of sodium nitrate, and transfer the mixed powder gradually to a small porcelain crucible containing 2 parts of sodium nitrate kept in a state of fusion at a not too strong heat. Oxidization of the sulphides ensues, attended with slight deflagration. The fused mass contains stannic oxide, sodium arsenate and antimonate, with sodium sulphate, carbonate, nitrate, and nitrite. Care must be taken not to raise the heat to such a degree, nor continue the fusion so long, as to lead to decomposition of the sodium nitrite, producing caustic soda, for this will cause the formation of sodium stannate soluble in water. Upon treating the mass with a little cold water, stannic oxide and acid sodium pyroantimonate remain undissolved, while sodium arsenate and the other salts are dissolved. If the filtrate is acidified with nitric acid, and heat is applied to remove carbonic and nitrous acids, the arsenic acid may be detected and separated, either with silver nitrate, according to § 156, 5, or with

a mixture of magnesium sulphate, ammonium chloride, and ammonia, according to § 156, 8, or as ammonium arseno-molybdate, as described in § 156, 9.

If the undissolved residue, consisting of stannic oxide and acid sodium pyroantimonate, after being washed once with cold water and three times with dilute alcohol, is digested with a little hydrochloric acid at a gentle heat in the hollow of a platinum crucible cover, the mass is either completely dissolved or, if the tin is present in a large proportion, a white residue is left undissolved. If, disregarding the latter, a fragment of zinc is now added, the compounds are reduced to the metallic state, and the antimony will at once reveal its presence by blackening the platinum. After the evolution of hydrogen has nearly stopped, if the remainder of the zinc is taken away, the zinc chloride solution is removed by careful decantation, and the contents of the cover are heated with some hydrochloric acid, the tin dissolves to stannous chloride, while the antimony, if present in considerable quantity, is left undissolved, partly in the form of black flakes. The tin may then be detected in the solution with mercuric chloride or with a mixture of ferric chloride and potassium ferricyanide, and the antimony, after solution in a little tartaric and nitric acids, may be tested with hydrogen sulphide. If the antimony has not been found with certainty by the foregoing reactions, a part of the hydrochloric acid solution obtained by treating the metals is evaporated to a small volume, a drop of hydrochloric acid is added, and a test is made with tin upon the platinum cover (see § 154, 9). As this method of detecting arsenic, tin, and antimony, in presence of each other, is adopted in the systematic course of analysis, the principle upon which it is based is here simply explained, and the details of the process will be found in the second part.

2. If the mixed sulphides, after being freed from the greater part of the adhering water by laying the filter containing them on blotting-paper, are treated with fuming hydrochloric acid, with application of a gentle heat, the sulphides of antimony and tin dissolve, while the sulphide of arsenic is left undissolved. The warming is continued until the hydrogen sulphide has escaped, then some water is

added, and the liquid filtered. If the sulphide of arsenic is treated (together with the filter, if very little is present) with concentrated nitric acid with the aid of heat, the resulting arsenic acid in the solution may be easily detected by means of ammonium molybdate (see § 156, 9). If the sulphide of arsenic is treated with ammonia, and the solution is evaporated to dryness, with the addition of a little piece of sodium carbonate, an arsenic mirror is readily obtained from the residue by treatment with potassium cyanide and sodium carbonate, in a stream of carbonic acid (see § 155, 13). The hydrochloric acid solution containing the tin and antimony is warmed for a short time with a bright rod of iron wire, and allowed to stand for ten or fifteen minutes. The antimony is thereby precipitated in the form of black flakes, while the stannic chloride is reduced to stannous chloride. A filtration is then made, and the filtrate is tested for tin, with mercuric chloride. The precipitated antimony may be further tested by dissolving it, after complete washing, in nitric acid containing a small amount of tartaric acid, and adding hydrogen sulphide water to the solution.

3. If the mixed sulphides are digested at a gentle heat with some solid, ordinary ammonium carbonate and water, arsenious sulphide dissolves, while the antimony and tin sulphides remain undissolved. But this separation is not quite absolute, as traces of antimony and tin sulphides are apt to pass into the solution, while some arsenious sulphide remains in the residue. The arsenious sulphide precipitating from the alkaline solution, upon acidifying the latter with hydrochloric acid, must, therefore (especially if consisting only of a few flakes), after washing, be treated with ammonia, the solution evaporated, with addition of a small quantity of sodium carbonate, and the residue fused with potassium cyanide in a stream of carbon dioxide, to make sure of the presence of arsenic by the production of an arsenical mirror. The residue, insoluble in ammonium carbonate, should be treated as directed in 2.

4. In the analysis of metallic alloys, stannic oxide and oxides of antimony and arsenic are often obtained together as a residue insoluble in nitric acid. It is best to fuse these with sodium hydroxide in a silver crucible, then soften the

mass with water, add one third of the volume of alcohol, filter off the acid sodium pyroantimonate remaining undissolved, and wash it with weak alcohol to which a few drops of a solution of sodium carbonate have been added. In the presence of much tin, it is advisable to treat the residue again in the same way, in order to extract all the tin. The filtrate is acidified with hydrochloric acid, then tin and arsenic are precipitated as sulphides in the heated solution, and these are most conveniently separated according to 2.

5. If very small amounts of arsenic are to be detected in the presence of much tin and antimony, it is advisable to distil the solution which contains the chlorides of the metals with not too small an amount of fuming hydrochloric acid and ferrous chloride or sulphate* (using a cooled receiver containing a little water), until about one fourth of the liquid has gone over, and to test the distillate with hydrogen sulphide (E. FISCHER, F. HUFSCHMIDT, A. CLASSEN). This method is less well adapted for detecting tin and antimony at the same time, because the distillation must then be continued and repeated until all the arsenic has been driven off, in which case, small quantities of antimony and tin may readily go over into the distillate; also, because the tin and antimony sulphides, precipitated with hydrogen sulphide from the residue from the distillation, are obtained mixed with much sulphur. A solution adapted for distillation is obtained from the sulphides of the metals by warming them with hydrochloric acid, with the addition of some potassium chlorate, or, still more conveniently, by suspending them in water and adding sodium peroxide (TH. POLECK).

6. Arsenic and antimony may be easily separated also by adding to 1 part of the solution 2 parts, or even a larger quantity, of hydrochloric acid of 1.2 sp. gr., and passing in hydrogen sulphide. The arsenic then separates as arsenious or arsenic sulphide, according to circumstances, while the antimony remains dissolved, and, after diluting with water, may be precipitated from the solution with hydrogen sulphide (O. KOEHLER, NEHER). Antimony may be

* Before these reagents can be used for the detection of minute amounts of arsenic, they should be put to test by the distillation method, to ascertain whether they are entirely free from arsenic.

separated from tin in a similar manner by diluting the liquid containing the tin as a stannic compound, with concentrated hydrochloric acid of 1.18 sp. gr., so that 1 part of this acid is present to 1 part * of water; because hydrogen sulphide precipitates from such a solution the antimony only, and not the tin (LOVITON). These two methods may be utilized for the separation of the three metals (NEHER).

7. It should be noted here that arsenic and antimony may be separated and distinguished by treating the mirror produced by MARSH'S process, with hydrogen sulphide, and separating the resulting sulphides by means of hydrochloric acid gas (see § 155, 10); but when antimony and arsenic are mixed as hydrogen compounds, they may also be separated by the following methods: *a.* First conduct the gases, mixed with an excess of hydrogen, through a tube containing glass splinters moistened with a dilute solution of lead acetate, to retain the hydrochloric acid and hydrogen sulphide gases, then in a slow stream into a solution of silver nitrate. Almost all the antimony in the gas falls down as black silver antimonide, Ag_3Sb, while the arsenic passes into the solution as arsenious acid, with reduction of the silver, and may be detected in the fluid as silver arsenite, by cautious addition of ammonia, or, after precipitating the excess of silver by hydrochloric acid, by means of hydrogen sulphide. Since, however, a little antimony always passes into the solution, the precipitate by hydrogen sulphide must not be considered as arsenious sulphide without further examination. The test may be made according to § 157, 2. In the precipitated silver antimonide, which is often mixed with much silver, the antimony may be most readily detected by heating the precipitate — thoroughly freed from arsenious acid and silver nitrate by boiling with water — with tartaric acid and water to boiling. This will dissolve the antimony alone, which may then be readily detected by means of hydrogen sulphide, in the solution acidified with hydrochloric acid (LASSAIGNE, A. W. HOFMANN). *b.* Conduct the gases, mixed with an excess of hydrogen, through a rather wide glass tube, 10 cm at least of which are filled with caustic potash in small pieces. The potash decomposes the hydrogen antimonide entirely, becoming coated with a

* Mr. H. A. Harper of Chicago advises using 2 parts of water.—H. L. W.

lustrous film of metal. The hydrogen arsenide is, on the contrary, scarcely at all decomposed, and may be detected readily on its exit from the tube by the production of stains or rings (see § 155, 10), or by its action on solution of silver nitrate (DRAGENDORFF). *c.* The stream of gas, very slowly evolved, is conducted through a mixture of 2 cc of silver solution (1 part silver nitrate and 24 parts water), 2 cc concentrated nitric acid, and 8 to 10 cc of water. When the black precipitate produced in the solution settles, the action may be considered as finished. Bromine-water in excess is now put into the flask containing the liquid and precipitate, or it is treated with hydrochloric acid with the addition of enough potassium chlorate so that chlorine is in excess. After some time, it is filtered, then tartaric acid, ammonium chloride, and ammonia are added in excess, and the arsenic, now present as arsenic acid, is precipitated as ammonium magnesium arsenate (see § 156, 8). After long standing, this is filtered off, the filtrate is acidified with hydrochloric acid, and the antimony is precipitated with hydrogen sulphide (E. REICHARDT). (If the liquid brought into contact with zinc in the presence of dilute sulphuric acid in the methods *a*, *b*, and *c*, also contained tin, the latter separates in the metallic state upon prolonged action of the zinc. If, therefore, the zinc solution is poured off, the residue is heated with hydrochloric acid, this is filtered, and mercuric chloride solution is added, the resulting precipitate of mercurous chloride shows the presence of tin). *d.* If a solution containing arsenious acid (but not arsenic acid) is brought into an apparatus evolving hydrogen from an alkaline solution (*e.g.*, one which contains potassium hydroxide, and arsenic-free aluminium foil or wire), and the gas is conducted through silver nitrate solution, any blackening taking place is decisive for arsenic alone, for under these conditions, hydrogen antimonide cannot form. *e.* If hydrogen arsenide or antimonide is allowed to act upon pure filter-paper which is moistened with a solution of silver nitrate, the moistened parts of the paper are colored. If, according to GUTZEIT, a solution is used which contains 1 part of silver nitrate to 1 part of water, a lemon-yellow stain is produced by hydrogen arsenide, which becomes black by being touched with water, while hydrogen antimonide colors

the periphery of the place touched with the silver solution, dark brownish-red to black. The inner part shows no color, or only a slight, gray coloration. Paper moistened with more dilute silver solution (*e.g.*, in the proportion 1 : 4) is blackened by both gases. These reactions, concerning which it must be remembered that hydrogen sulphide and phosphide give similar colorations, have undergone various criticisms and modifications since they were introduced into the German pharmacopœia. RITSERT recommends the use of an ammoniacal silver solution. A paper moistened with this becomes dull brown to black from the most minute amount of hydrogen arsenide. The reaction is not influenced by aqueous or acid vapors nor by the action of the paper, but it is interfered with by the presence of hydrogen sulphide and phosphide, as well as by that of hydrogen antimonide, the latter also giving brown to black stains. A complete summary and critical testing of the methods referred to have been given by H. BECKURTS.* It must suffice to mention this here. *f.* If pure filter-paper is spotted with a drop of a saturated alcoholic solution of mercuric chloride, this is allowed to dry superficially, the operation is repeated four or five times, and hydrogen arsenide is allowed to act upon paper thus prepared, a stain, at first light yellow, but becoming orange-colored upon longer action, is produced. Hydrogen antimonide produces no stain when acting in very small quantity, but it gives a brown to grayish-black color when the amount is larger. If the stain is occasioned by both hydrogen compounds, that formed by hydrogen arsenide may be detected, if not too much hydrogen antimonide has acted, by moistening the stain, after cutting it out, with 80 per cent alcohol in a watch-glass. The coloration produced by hydrogen antimonide disappears after standing for a while, and allows the yellow color produced by hydrogen arsenide to be recognized (FLÜCKIGER, LOHMANN).

8. If saturated hydrogen sulphide water is added to a solution acidified with hydrochloric acid which contains arsenic and antimonic acids, and after a few minutes, a stream of air is passed through the liquid in order to remove the excess of hydrogen sulphide, the precipitate contains all the

* Pharmac. Centralhalle, 1884, No. 17.

antimony as antimonic sulphide, but no arsenic. The latter can then be precipitated from the filtrate, when warmed to 70°, by passing in hydrogen sulphide (BUNSEN).

9. The attention of chemists who are expert in flame-reactions should also be called to the method of BUNSEN,* which is designed to detect all three metals in the precipitate of their sulphides, by means of flame-reactions and blowpipe tests. Reference only will be here made to the methods, partly microscopic, of H. HAGER,† which are chiefly intended for the rapid detection of arsenic in pharmaceutical preparations.‡

10. *Stannous and stannic compounds* may be detected in presence of each other, by testing one portion of the solution for the first, with mercuric chloride, auric chloride, or a mixture of potassium ferricyanide and ferric chloride, and another portion for stannic compounds, by pouring it into a concentrated, hot solution of sodium sulphate. For the last test, the solution must not contain much free acid.

11. *Antimonious oxide* in presence of *antimonic acid* may be identified by the reaction described in § 154, 11. *Antimonic acid* in presence of *antimonious oxide* is detected by heating the oxide (which must be free from other bodies) with hydrochloric acid and potassium iodide (see § 154, 2 and 3), or by adding to the solution, mixed with concentrated sulphuric acid, after cooling, a drop of a solution of diphenylamine in concentrated sulphuric acid, whereby, in presence of antimonic acid, a deep blue coloration of the liquid results. This reaction, however, is only conclusive for antimonic acid when other substances giving the same coloration with diphenylamine, such as nitric acid, chromic acid, etc., are not present.

12. *Arsenious acid* and *arsenic acid* in the same solution may be distinguished by means of silver nitrate. If the precipitate contains little arsenate and much arsenite of silver, it

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* Zeitschr f. analyt. Chem., 5, 378.

† Pharmac. Centralhalle, 1884, p. 265 and p 277.

‡ In relation to other methods proposed for the separation of antimony, tin, and arsenic, see F. W. CLARKE, Zeitschr. f. analyt. Chem., 9, 487; BERGLUND, *ibid.*, 23, 537, and 24, 221; LESSER, *ibid*, 27, 218; J. CLARK, Chem. Centralbl. 1892, I, 965. See also, for the separation of antimony and tin, LUCKOW, Zeitschr. f analyt. Chem., 26, 13; CARNOT, *ibid.*, 27, 651; WARREN, Chem. Centralbl., 1888, p. 645.

is necessary, in order to identify the former, to add cautiously, drop by drop, most highly dilute nitric acid, which dissolves the yellow silver arsenite first. A still safer way to detect small quantities of arsenic acid in presence of arsenious acid is to precipitate the former with a mixture of magnesium sulphate, ammonium chloride, and ammonia (§ 156, 8), by which means an actual separation of the two acids is effected. Arsenious acid may be recognized in presence of arsenic acid by the *immediate* precipitation by hydrogen sulphide of the moderately acidified solution in the cold, which is not the case with arsenic acid; also, by the fact that arsenious acid alone evolves hydrogen arsenide when brought into solution of sodium hydroxide which is acting upon aluminium. Arsenious acid is also readily detected by its reduction of cupric oxide in alkaline solution, and by the separation of metallic silver, by boiling the ammoniacal solution of the silver salts. To ascertain the degree of sulphuration of arsenic in a sulphur salt, boil the alkaline solution of the salt under examination (after the extraction with carbon disulphide of any sulphur that may be present) with bismuth hydroxide, filter off the bismuth sulphide formed, and test the filtrate for arsenious and arsenic acids. To distinguish between the arsenious and arsenic sulphides, first completely extract the sulphur which may be present, by means of carbon disulphide, then dissolve the residue in ammonia, add immediately silver nitrate in excess, filter off the silver sulphide, and observe whether arsenite or arsenate of silver is formed upon addition of ammonia. It should be observed that a portion of the arsenic is to be found with the bismuth sulphide and silver sulphide in the two tests last mentioned (WAITZ).

13. GOLD and PLATINUM may be separated from TIN, ANTIMONY, and ARSENIC, by boiling their solutions in an excess of sodium hydroxide with chloral hydrate. The resulting precipitate contains all the gold and platinum free from the other metals.

Special Reactions of the Rarer Metals of the Sixth Group.

§ 158.

1. GERMANIUM, Ge. (*Germanic Oxide*, GeO_2.)

Up to the present time, GERMANIUM has been found only in argyrodite, euxinite, and canfieldite, and in very small quantity. It forms two oxides; germanious oxide, GeO, and germanic oxide. The metal is obtained as a powder by igniting the oxides in hydrogen, and this may be fused under borax to a grayish-white regulus with a metallic luster. This has a specific gravity of 5.469, is easily pulverized, and is permanent in the air. Germanium volatilizes at a bright red heat, yielding a sublimate consisting of small crystals. It is insoluble in hydrochloric acid, and it is converted by nitric acid into white germanic oxide, and by concentrated sulphuric acid, upon heating, into a white sulphate soluble in water. Aqua regia dissolves the metal readily to chloride; concentrated potassium hydroxide solution does not attack it, but it gives potassium germanic oxide upon fusion with potassium hydroxide, the action being accompanied by deflagration. Germanic oxide is formed by burning the metal in oxygen, by roasting germanic sulphide, by treating the metal with nitric acid, and by decomposing the chloride with water, etc. It is a white, dense powder, difficultly soluble in water, which may be heated to bright redness without undergoing any change, and dissolves but slightly in acids. The alkali-metal hydroxides and carbonates dissolve it when they are fused with it, and convert it into compounds that are soluble in water. Germanic chloride, $GeCl_4$, obtained by igniting the metal or the sulphide in a stream of chlorine, forms a mobile, colorless liquid, boiling at 80°, which is volatile even at ordinary temperatures, and is decomposed by water, with formation of the oxide, which partially separates. If the aqueous solution of the chloride is acidified with hydrochloric acid, and evaporated to dryness upon the water-bath, the chloride volatilizes completely.

From acid solutions containing germanic salts, *hydrogen sulphide* precipitates germanic sulphide, GeS_2, in the form of a white, voluminous precipitate. This is somewhat soluble in water, even in hydrogen sulphide water. In order to obtain it pure, therefore, it should first be washed with hydrochloric or sulphuric acid saturated with hydrogen sulphide, then with alcohol saturated with the same gas, and finally with ether. After drying, it forms a soft, white powder. If it is heated in a stream of carbonic acid, an odor is produced resembling very dilute acrolein, and the sulphide shrinks greatly and assumes a yellowish or grayish-yellow color. It volatilizes upon being heated to a bright red heat. Germanic sulphide dissolves readily in *ammonium sulphide*, and

a sufficient excess of acid precipitates it unchanged and white in color from the solution (characteristic reaction). Germanic sulphide is also readily dissolved by potassium hydroxide and by ammonia. Aqua regia dissolves it, with separation of sulphur. Nitric acid changes it into oxide containing sulphuric acid and mixed with sulphur. If germanic sulphide is heated in a stream of hydrogen, germanious sulphide, GeS, is produced at first, with the formation of hydrogen sulphide. Upon further heating, this is partly reduced to germanium. From solutions of germanium salts, *zinc* separates the metal slowly in the form of a dark brown slime. Before the *blowpipe*, when heated without an alkaline flux in the reducing flame, germanic oxide gives the fused metal, with the formation at the same time of a white coating of the oxide. *Borax* and *salt of phosphorus* dissolve the oxide abundantly, both in the oxidizing and the reducing flames, giving colorless glasses which are not changed even by heating with tin. *Non-luminous flames* are not colored by germanium compounds, and consequently they cannot be detected by means of the *spectroscope*. The detection of the small amount of germanium in argyrodite may be effected by heating the mineral in an atmosphere of hydrogen sulphide or illuminating-gas. A sublimate is thus obtained, similar to antimony sulphide, which shows very characteristic forms under the microscope, and which may be subjected to further tests in the wet way (HAUSHOFER*).

§ 159.

2. IRIDIUM, Ir. (*Iridic Oxide*, IrO_2.)

IRIDIUM occurs in combination with platinum and other metals in the platinum ores, but more especially as osmiridium. Alloyed with platinum, it has of late been employed for crucibles, etc. Iridium resembles platinum, but it is brittle, fuses with extreme difficulty, and its specific gravity is 22.4. In the compact state, or reduced at a red heat by hydrogen, it dissolves in no acid, not even in aqua regia (difference from gold and platinum). Reduced in the moist way, *e.g.*, by formic acid, or largely alloyed with platinum, it dissolves in aqua regia to tetrachloride, $IrCl_4$. In a state of fusion, *potassium disulphate* oxidizes, but does not dissolve it (difference from rhodium). It oxidizes by fusion with *sodium hydroxide* with access of air, or by fusion with sodium nitrate. The compound of iridious oxide, Ir_2O_3, with soda which is formed in this process, dissolves partially in water; and by heating with aqua regia, it gives a deep black-red solution of iridic chloride, $IrCl_4$, and sodium chloride.

If iridium powder is mixed with sodium chloride, the mixture heated

*Sitzungsber. der Münchener Akademie, 1887, p. 133; Chem. Centralbl., 1888, p. 867.

to incipient redness, and treated with *chlorine gas*, sodium iridic chloride is formed, which dissolves in water to a deep red-brown fluid. *Potassium hydroxide*, added in excess, colors the solutions greenish, a little brownish-black potassium iridic chloride precipitating at the same time. If the solution is heated, and exposed some time to the air, it acquires at first a reddish tint, then becomes violet, and with absorption of oxygen, it changes afterwards to blue (CLAUS, characteristic difference from platinum). If the solution is now evaporated to dryness, and the residue treated with water, a colorless fluid is obtained, while a blue deposit of iridic oxide, IrO_2, is left undissolved. If the solution of iridic chloride is heated with sulphuric acid until vapors of sulphuric acid escape, and the residue is treated with water at the boiling temperature, a clear solution of a green or sometimes blue or violet color is usually obtained. If this is neutralized with potassium hydroxide and boiled from fifteen to thirty minutes, finally with the addition of an excess of potassium hydroxide, an oxide separates, which dissolves in dilute sulphuric acid with a bright violet color. If solid *ammonium nitrate* is added in small portions to the iridium salt heated with sulphuric acid, as mentioned above, as soon as the vapors of sulphuric acid have stopped coming off, after removing the dish from the source of heat, a blue or sometimes an emerald-green mass is obtained, which, if the operation is interrupted before all the ammonium nitrate has been decomposed, dissolves in water to a blue liquid. The presence of foreign metals naturally interferes with the delicacy of the reaction. If iridic chloride is heated directly with ammonium nitrate and ammonium chloride, added at intervals, a rose-red mass, instead of a blue one, is obtained, from which a rose-red powder separates upon treatment with very little water (LECOQ DE BOISBAUDRAN). *Hydrogen sulphide* at first colors solutions of iridic chloride olive-green, and iridious chloride, Ir_2Cl_6, is formed, with separation of sulphur; afterwards, brown iridious sulphide, Ir_2S_3, is precipitated. *Ammonium sulphide* produces the same precipitate, which redissolves readily in an excess of the precipitant. *Potassium chloride* precipitates potassium iridic chloride as a blackish-red crystalline powder, insoluble in a concentrated solution of potassium chloride. *Ammonium chloride* precipitates from concentrated solutions, ammonium iridic chloride in the form of a dark red powder, consisting of microscopic octahedrons, insoluble in concentrated solution of ammonium chloride. This double salt, and also the corresponding potassium compound, especially when in hot solution, are turned olive-green by *potassium nitrite*, owing to the formation of potassium or ammonium iridious chloride: $2K_2IrCl_6 + 2KNO_2 = 6KCl.Ir_2Cl_6 + 2NO_2$. This double salt crystallizes out on cooling. On heating or evaporating the green solution with an excess of potassium nitrite, it turns yellow, and when boiled deposits a white precipitate, which is hardly soluble in water and hydrochloric acid (essential difference and basis of a method of separation from platinum, GIBBS). If the iridic ammonium chloride is dissolved in water by boiling, and *oxalic acid* is added, a reduction to the iridious salt takes place, and on this account, the solution remains clear on cooling

(difference from platinum, C. LEA). If *stannous chloride* is added to iridic chloride and the solution is boiled, then an excess of potassium hydroxide is added and the mixture is boiled again, a leather-colored precipitate is formed. *Ferrous sulphate*, *oxalic acid*, and *sulphurous acid* do not precipitate iridium (means of separating iridium from gold); but *zinc* separates black iridium. If iridic oxide is suspended in a solution of *potassium sulphite*, and this is saturated with *sulphurous acid* and boiled, with renewal of the evaporating water, till all the free sulphurous acid is expelled, the whole of the iridium is converted into insoluble iridic sulphite (any platinum which may be present will remain dissolved as platinous potassium sulphite, C. BIRNBAUM). Ignited with *sodium carbonate* in the upper oxidizing flame, compounds of iridium yield the metal, which when triturated is gray, devoid of luster, and without ductility. Concerning the microscopic detection of iridium, see BEHRENS, Zeitschr. f. analyt. Chem., **30**, 154.

§ 160.

3. MOLYBDENUM, Mo. (*Oxides of Molybdenum.*)

MOLYBDENUM is not largely disseminated in nature, and is found only in moderate quantities, more especially as molybdenum sulphide and as lead molybdate (yellow lead ore). From the use of ammonium molybdate as a means of detecting and determining phosphoric acid, molybdenum has acquired considerable importance in practical chemistry. MOLYBDENUM is tin-white and hard; when heated in the air, it oxidizes; and it is easily soluble in nitric acid and in aqua regia, as well as in concentrated sulphuric acid. It fuses with extreme difficulty. The MONOXIDE, MoO, and the SESQUIOXIDE, Mo_2O_3, are black; while the dioxide, MoO_2, is dark brown or dark violet. When heated in the air or treated with nitric acid, all of these are converted into MOLYBDIC ACID, MoO_3. This is a white, porous mass, which separates into fine scales in water, and dissolves to a slight extent. It fuses at a red heat; in close vessels, it volatilizes only at a very high temperature; while in the air, it volatilizes easily at a red heat, and sublimes to transparent laminæ and needles. On igniting it in a current of hydrogen, it is first converted into the dioxide, and afterwards, by strong and long-continued heating, into the metal. The non-ignited acid dissolves in acids. When heated to redness in vapor of carbon tetrachloride or in a mixture of chlorine and carbon monoxide, molybdic acid yields volatile chlorides (QUANTIN). The solutions are colorless; but the hydrochloric solution is colored by contact with *zinc* soon, and on addition of *stannous chloride* immediately, the color being blue, green, or brown, according to the proportion of reducing agent and the concentration of the fluid. Digested with *copper*, the sulphuric acid solution turns blue, and the hydrochloric acid solution, brown. The reaction often requires some time. A solution of *ferrous sulphate* acidified with sulphuric acid colors acid solutions per-

manently blue. If *sodium hypophosphite* and *sulphurous acid* are added to an acid solution of molybdic acid, a blue precipitation or only a blue coloration of the liquid results, according to the amount of molybdenum present. Slight warming hastens the appearance of the reaction (MILLARD). In solutions acidified with hydrochloric acid, *potassium ferrocyanide* produces a reddish-brown precipitate. *Tincture of galls* as well as *tannin* color solutions of alkaline molybdates deep red with a brown tint, and if hydrochloric acid is now added, a brown precipitate or coloration results. A little *hydrogen sulphide* colors acid solutions blue, while more gives a brownish-black precipitate. The fluid over the latter at first appears green, but after being allowed to stand for some time, and heated, additional quantities of hydrogen sulphide being repeatedly conducted into it, the whole of the molybdenum present separates ultimately, though slowly, as brownish-black molybdenum trisulphide, MoS_3. The precipitate dissolves in sulphides of the alkali metals. Acids reprecipitate molybdenum trisulphide from the sulphur salts thus formed, and the application of heat promotes the separation. Boiling oxalic acid solution does not attack molybdenum sulphide (means of separation from tin sulphide produced in the wet way, which dissolves in it, CLARKE). By heating to redness in the air, or by heating with nitric acid, molybdenum sulphide is converted into the acid. If *potassium sulphocyanide* and a little hydrochloric acid are added to a solution containing molybdic acid, it is not colored; but if some *zinc* is added, reduction takes place, and in consequence of the formation of a sulphocyanide corresponding to the dioxide or also to the sesquioxide, the liquid is colored carmine-red. The addition of phosphoric acid does not destroy the reaction (difference from ferric sulphocyanide). Upon shaking the red liquid with ether, the sulphocyanides are dissolved in the latter, and there is consequently formed a red layer of ether (C. D. BRAUN). If *hydrogen peroxide* is added to an acid solution of molybdic acid, a yellow-colored liquid results, the color of which is not taken up by ether upon shaking with the latter (SCHÖN, WERTHER, BÄRWALD). When vanadium or titanium compounds are present at the same time, the reaction is not applicable.

Molybdic acid dissolves readily in solutions of *alkalies* and *alkali carbonates*. From concentrated solutions, *nitric acid* or *hydrochloric acid* throws down molybdic acid, which redissolves in a large excess of the precipitant. The solutions of molybdates of the alkali metals are colored yellow by *hydrogen sulphide*, and give afterwards, upon addition of acids, a brownish-black precipitate. If a solution of molybdic acid in excess of ammonia is mixed with *yellow ammonium sulphide*, and boiled for some time, a dark red liquid of great depth of color is formed, in addition to a brownish-black precipitate unless a very large excess of ammonium sulphide is present. For the deportment of molybdic acid with *orthophosphoric acid* and ammonia, see § 172, 10.

If a little concentrated sulphuric acid is dropped upon a trough-shaped piece of platinum foil, a small amount of molybdic acid or of a molybdate is added in the form of powder, and the mixture is

then heated to copious fuming, allowed to cool, and a little alcohol is added or the platinum foil breathed upon repeatedly, an intense BLUE COLORATION OF THE SULPHURIC ACID is produced (v. KOBELL, SCHÖN, MASCHKE). In the presence of antimonic acid or of much stannic oxide, the mixture must be evaporated with phosphoric acid before it is heated with sulphuric acid (MASCHKE). When molybdic acid is heated on charcoal in the *oxidizing flame*, it is volatilized, and the charcoal becomes coated with a yellow powder, often crystalline, which becomes white upon cooling. In the *reducing flame*, metallic molybdenum is produced, which is obtained as a gray powder upon washing away the carbon. In the oxidizing flame, molybdenum sulphide yields sulphurous acid, and molybdic acid which coats the charcoal. If molybdic acid or a molybdate is heated for a short time with sodium carbonate in a spiral of platinum, the mass is dissolved in a few drops of water with the aid of heat, and the solution is soaked up with strips of filter-paper, these allow the recognition of molybdenum by touching them with hydrochloric acid and potassium ferrocyanide, with stannous chloride, and also with ammonium sulphide and hydrochloric acid (BUNSEN). If molybdic acid is heated with an equal quantity of sulphur iodide* upon an artificially prepared gypsum plate, in the oxidizing flame of the blow-pipe, an ultramarine-blue coating is obtained (WHEELER and LÜDEKING). Concerning the microchemical detection of molybdenum, compare HAUSHOFER, p. 97; BEHRENS, Zeitschr. f. analyt. Chem., **30**, 168.

§ 161.

4. TUNGSTEN, W. (*Oxides of Tungsten.*)

TUNGSTEN does not occur widely disseminated in nature, and only in moderate amount. The most common tungsten minerals are scheelite (calcium tungstate) and wolframite (ferrous and manganous tungstate). Tungsten, produced by the reduction of tungstic acid by hydrogen at a strong red heat, is an iron-gray powder, which is very difficultly fusible. The powder when ignited in the air gives tungstic acid, WO_3. When heated in dry chlorine gas, free from air, it is converted into the blackish-violet tungstic chloride, WCl_6, which may be sublimed, and generally contains lower chlorides and sometimes oxychlorides. This chloride is decomposed by heating with water, forming hydrated tungstic acid. Tungstic chloride is also obtained by heating tungstic acid to redness in the vapor of carbon tetrachloride or in a mixture of chlorine and carbon monoxide (QUANTIN). Acids, even aqua regia, dissolve metallic tungsten but little or not at all. It is also insoluble in potassium hydroxide solution, but it is dissolved by this reagent when an alkaline hypochlorite is mixed with it. TUNGSTEN DIOXIDE, WO_2, is brown, and by intense igni-

*This is prepared by fusing together 40 parts of iodine and 60 parts of sulphur, and pulverizing the mass.

tion, with free access of air, it is converted into tungstic acid. TUNGSTIC ACID is lemon-yellow when cold, dark orange when hot, fixed, and insoluble in water and acids. With water and with bases, it forms two series of compounds: tungstates and metatungstates. By fusing tungstic acid with potassium disulphate, and treating the fused mass with water, an acid solution is obtained, which contains no tungstic acid. After the removal of this solution, the residue, consisting of potassium tungstate and a large excess of tungstic acid, completely dissolves in water containing ammonium carbonate (difference and means of separating tungstic from silicic acid). ALKALI-METAL TUNGSTATES soluble in water are formed readily by fusion with alkali-metal carbonates, but with more difficulty by boiling with solutions of the same. *Hydrochloric acid*, *nitric acid*, and *sulphuric acid*, when added in sufficient quantity, produce in solutions of these tungstates white precipitates, which turn yellow on boiling, and are insoluble in an excess of the acids (difference from molybdic acid), but soluble in ammonia. They also dissolve, after pouring off the acid, upon protracted treatment with water. Upon evaporating with an excess of nitric acid to dryness, heating the residue to 120°, and treating the latter, without warming, with a solution of ammonium nitrate containing some nitric acid, the tungstic acid remains almost entirely undissolved (N. J. TRAM, A. ZIEGLER). *Phosphoric acid* does not produce precipitates, but rapidly changes tungstic acid into metatungstic acid, in consequence of which, it prevents the precipitation by other acids. *Barium chloride*, *calcium chloride*, *lead acetate*, *silver nitrate*, and *mercurous nitrate* produce white precipitates. *Potassium ferrocyanide*, with addition of some acid, colors the fluid deep brownish-red, and after some time produces a precipitate of the same color. *Tincture of galls* and also *tannin*, with a little acid added, produce a brown color or precipitate. *Hydrogen sulphide* scarcely precipitates acid solutions. *Ammonium sulphide* fails to precipitate solutions of alkali-metal tungstates, but upon acidifying the solution containing an excess of ammonium sulphide, light brown trisulphide, WS_3, mixed with sulphur, precipitates, which is slightly soluble in pure water, but is practically insoluble in water containing salts. *Stannous chloride* produces a yellow precipitate, which on acidifying with hydrochloric acid, and applying heat, acquires a beautiful blue color (highly delicate and characteristic reaction). If solutions of alkali tungstates are mixed with hydrochloric acid, or better still, with an excess of phosphoric acid, and *zinc* is added, the fluid acquires a beautiful blue color. The blue color produced in the hydrochloric acid solution changes transiently into red, and then becomes brownish-black. Also, upon the addition of *sodium hypophosphite* and *sulphurous acid* to a solution of an alkaline tungstate somewhat acidified with sulphuric acid, a solution colored deep blue is obtained upon gentle warming. *Ferrous sulphate* gives an ochre-colored precipitate, which does not become blue with acids (difference from molybdic acid). The METATUNGSTATES are mostly soluble in water. Upon protracted boiling, sulphuric, hydrochloric, and nitric acids separate from the solutions the hydrate of ordinary tungstic acid. Fusing *sodium meta-*

phosphate dissolves tungstic oxide. The bead, exposed to the oxidizing flame, appears clear, varying from colorless to yellowish; while in the reducing flame, it acquires a pure blue color, and upon addition of ferrous sulphate, a blood-red color. By mixing tungstic acid with very little *sodium carbonate*, and exposing in the cavity of the charcoal support to the reducing flame, tungsten in powder is obtained, which may be separated by washing. If tungstic acid is fused in the *platinum spiral* with sodium carbonate, the mass is warmed with a few drops of water, and the solution soaked up with strips of filter-paper, the latter give a means of detecting tungstic acid by the yellow color produced by moistening them with hydrochloric acid and warming, and by the blue color produced by touching them with stannous chloride and warming. Ammonium sulphide does not color the paper, either alone or after the addition of hydrochloric acid, but it assumes a blue or green color upon warming (BUNSEN). Upon heating with *sulphur iodide* upon a gypsum tablet in the oxidizing blowpipe flame (compare § 160), tungstic acid yields a pale greenish-blue coating (WHEELER and LÜDEKING). The tungstates which are insoluble in water may, most of them, be decomposed by digestion with acids. Wolframite, which strongly resists the action of acids, is fused with alkali-carbonate, when water will dissolve from the mass the alkali tungstate formed. Concerning the microchemical detection of tungstic acid, see HAUSHOFER, p. 141; BEHRENS, Zeitschr. f. analyt. Chem., 30, 169.

§ 162.

5. TELLURIUM, Te. (*Oxides of Tellurium.*)

TELLURIUM is not widely disseminated, and is found in small quantities only, in the native state or alloyed with other metals, or as tellurous acid. It is a white, brittle, readily fusible metal, which may be sublimed in a glass tube. Heated in the air, it burns with a greenish-blue flame, emitting thick, white fumes of tellurous acid. Tellurium is insoluble in hydrochloric acid, but dissolves readily in nitric acid to tellurous acid, TeO_2. Tellurium in powder dissolves in cold, concentrated sulphuric acid to a purple-colored fluid, from which it separates again upon addition of water. If the concentrated solution is heated, it becomes decolorized, and the greater part of the sulphate of tellurous acid, which is formed, separates. TELLUROUS ACID is white; at a gentle red heat, it fuses to a yellow fluid, and it is volatilized by strong ignition in the air, forming no crystalline sublimate. The anhydrous acid dissolves readily in hydrochloric acid, sparingly in nitric acid and dilute sulphuric acid, freely in solution of potassium hydroxide, slowly in ammonia, and barely in water. Hydrated tellurous acid is white, perceptibly soluble in cold water, and dissolves easily in hydrochloric acid and in nitric acid. Addition of water to the acid solutions throws down the white hydroxide, and from the undiluted nitric acid solution nearly all the tellurous acid separates after some

time as a crystalline precipitate. From the hydrochloric acid solution, *alkalies* and *alkali carbonates* throw down a white hydroxide, which is soluble in an excess of the precipitant. *Hydrogen sulphide* produces in acid solutions a brown precipitate of tellurous sulphide, TeS_2 (in color like stannous sulphide), which dissolves very freely in ammonium sulphide. From acid solutions, *stannous chloride* and also *zinc* precipitate black, metallic tellurium. *Sulphurous acid* and *sodium sulphite* precipitate the metal in this way only in the presence of hydrochloric acid. If a solution of tellurous acid in an excess of potassium or sodium hydroxide is heated with addition of *grape-sugar*, there is also a precipitation of metallic tellurium (STOLBA). Tellurous acid produces a white precipitate in a mixture of *magnesium chloride*, *ammonium chloride*, and *ammonia*. This precipitate is not crystalline (difference from selenious acid, HILGER, v. GERICHTEN). TELLURIC ACID, TeO_3, is formed by fusing tellurium or compounds of tellurous acid with mixtures of alkaline nitrates and carbonates. The mass is soluble in water, the solution remains clear upon acidifying it with hydrochloric acid in the cold, but upon boiling, it evolves chlorine, and tellurous acid is formed, which may be precipitated by water if the excess of acid is not too great.

If tellurium, its sulphide, or an oxygen compound of the metal, is fused with *potassium cyanide* in a stream of hydrogen, potassium tellurocyanide is formed. The fused mass dissolves in water, but a current of air throws down from the solution the whole of the tellurium (difference and means of separation from selenium). If finely pulverized tellurium or tellurium ore, *e.g.*, gold telluride, is covered with a little water in a porcelain dish, a little mercury is added, and then a little sodium amalgam is brought upon this, the water is immediately colored beautifully violet in consequence of sodium telluride going into solution (G. KÜSTEL). When tested in the dry way by BUNSEN'S method (p. 31), the compounds of tellurium give a grayish-blue color in the upper reducing flame, while the upper oxidizing flame appears green. The volatilization is unaccompanied by any odor. The *incrustation produced by reduction* is black, with a blackish-brown edge, and gives a crimson solution when heated with concentrated sulphuric acid. The *incrustation of oxide* is white, and scarcely visible; but stannous chloride colors it black, metallic tellurium being separated. When heated with *sodium carbonate* in the *stick of charcoal*, compounds of tellurium yield sodium telluride, which when placed on clean silver and moistened produces a black stain, and when treated with hydrochloric acid (in the presence of enough tellurium) gives an odor of hydrogen telluride, with separation of tellurium. Concerning the microscopic detection of tellurium, see HAUSHOFER, p. 124; BEHRENS, Zeitschr. f. analyt. Chem., 30, 167.

§ 163.

6. Selenium, Se. (*Oxides of Selenium.*)

Selenium occurs rarely in nature, in the form of selenides of metals. It is found occasionally in pyrites, and, in consequence of this, also in sulphuric and hydrochloric acids. It resembles sulphur in some respects, and tellurium in others. Fused selenium is grayish-black, volatilizes at a high temperature, and may be sublimed. Heated in the air, it burns to selenious oxide, SeO_2, exhaling a characteristic smell of decaying radish. Selenium is soluble in carbon disulphide. The solution in contact with mercury produces black selenide of mercury. Cold concentrated sulphuric acid dissolves selenium to a dark green liquid, without oxidizing it, and upon diluting the solution, the selenium falls down in red flakes. Upon boiling with concentrated sulphuric acid, it dissolves with oxidation to selenious acid. Nitric acid and aqua regia also dissolve selenium to selenious acid. This volatilizes at about 200°, forming a deep yellow gas. Sublimed selenious acid appears in the form of white, four-sided needles, and hydrated selenious acid, in the form of crystals resembling those of potassium nitrate. Both the anhydride and the hydrated acid dissolve readily in water, forming strongly acid fluids. Of the normal salts, only those with the alkali metals are soluble in water; the solutions have alkaline reactions. Most of the selenides dissolve readily in nitric acid, but the lead and silver salts dissolve with difficulty. In solutions of selenious acid or of selenites in the cold (in presence of free hydrochloric acid), *hydrogen sulphide* produces a yellow precipitate of a mixture of finely divided selenium and sulphur, which upon heating turns reddish-yellow, and is soluble in ammonium sulphide. *Barium chloride* produces (after neutralization of the free acid, should any be present) a white precipitate of barium selenite, which is soluble in hydrochloric acid and in nitric acid. *Sulphurous acid* precipitates red selenium from acid solutions, and also even from sulphuric acid solutions (difference from tellurium). *Stannous chloride* gives the same precipitate in hydrochloric and sulphuric acid solutions. *Metallic copper*, when placed in a warm solution of selenious acid containing hydrochloric acid, immediately becomes coated black; and if the fluid remains long in contact with the copper, it turns light red from separation of selenium (Reinsch). Selenious acid produces in a mixture of *magnesium chloride*, ammonium chloride, and ammonia, usually only after some time, a colorless, crystalline precipitate of magnesium selenite, which is soluble in acids (Hilger, v. Gerichten). Selenic acid, SeO_3, is produced by heating selenium or its compounds with mixtures of alkaline carbonates and nitrates. The mass is soluble in water, and the solution remains clear upon being acidified with hydrochloric acid. When boiled with the latter, it evolves chlorine, selenic acid being converted into selenious acid. If selenium or one of its compounds is fused with *potassium cyanide* in a

stream of hydrogen, potassium selenocyanide is obtained, from which the selenium is not eliminated by the action of the air (as is the case with tellurium). It separates, however, upon long-continued boiling, after addition of hydrochloric acid. When tested according to p. 31, compounds of selenium give a *blue color to the flame*, and by *volatilization* and combustion of the vapor, the characteristic odor of decaying radish is emitted. The *incrustation produced by reduction* is brick-red to cherry-red, and gives a dirty green solution with concentrated sulphuric acid. The *incrustation of oxide* is white, and when moistened with stannous chloride becomes red from separated selenium. In the *charcoal stick* with *sodium carbonate*, sodium selenide is formed, which when placed on silver and moistened produces a black stain, and when treated with acids yields hydrogen selenide. Heated with sulphur iodide in the oxidizing flame of the blowpipe, upon a gypsum tablet (compare § 160), selenious acid gives a reddish-brown coating (WHEELER and LÜDEKING). Concerning the microscopic detection of selenium, see HAUSHOFER, p. 116; BEHRENS, Zeitschr. f. analyt. Chem., 30, 167.

To separate selenium from tellurium, heat the solution of tellurous and selenious acids in concentrated sulphuric acid with a fourfold volume of a moderately strong, aqueous solution of sulphurous acid, warm for some time, filter off the separated selenium, and heat with hydrochloric acid with the addition of more sulphurous acid, in order to precipitate the tellurium (DIVERS and SCHIMOSE).

B.—DEPORTMENT OF THE ACIDS AND THEIR RADICALS.

§ 164.

The reagents which serve for the detection of the acids are divided, like those used for the detection of the metals, into GENERAL REAGENTS, *i.e.*, such as indicate the GROUP to which the acid under examination belongs; and SPECIAL REAGENTS, *i.e.*, such as serve to effect the identification of the INDIVIDUAL ACIDS. The groups of acids cannot be defined with the same degree of precision as those into which the bases are divided.

The two principal groups are the INORGANIC and ORGANIC ACIDS. This division is based upon those characteristics by which the ends of analysis are most easily attained, regardless of theoretical considerations. In fact, this distinction is

based upon the behavior at a high temperature, and those acids are called *organic* of which the salts (particularly those of an alkali or an alkali-earth metal) are decomposed upon ignition, with separation of carbon. This criterion has the advantage, that a most simple preliminary experiment at once determines the class to which an acid belongs. The salts of organic acids with alkali or alkali-earth metals are converted into carbonates when heated to redness.

Before proceeding to the special study of the several acids, a general view of all of them, classified in groups, is here given.

I. Inorganic Acids.

FIRST GROUP:

Division *a*. *Chromic acid* (sulphurous and thiosulphuric acids, iodic acid).

Division *b*. *Sulphuric acid* (hydrofluosilicic acid).

Division *c*. *Phosphoric acid*, *boric acid*, *oxalic acid*, *hydrofluoric acid* (phosphorous acid).

Division *d*. *Carbonic acid*, *silicic acid*.

SECOND GROUP:

Chlorine and *hydrochloric acid*; *bromine* and *hydrobromic acid*; *iodine* and *hydriodic acid*; *cyanogen* and *hydrocyanic acid*, together with *hydroferro-* and *hydroferricyanic acids*, as well as *hydrosulphocyanic acid*; *sulphur* and *hydrosulphuric acid* (*hydrogen sulphide*) (nitrous acid, hypochlorous acid, chlorous acid, hypophosphorous acid).

THIRD GROUP:

Nitric acid, *chloric acid* (perchloric acid).

II. Organic Acids.

FIRST GROUP:

Oxalic acid, *tartaric acid*, *citric acid*, *malic acid* (racemic acid).

SECOND GROUP:

Succinic acid, benzoic acid, salicylic acid.

THIRD GROUP:

Acetic acid, formic acid (lactic acid, propionic acid, butyric acid).

The acids printed in italics are more frequently met with in the examination of minerals, waters, ashes of plants, industrial products, articles of food and luxury, medicines, etc.; while the others occur more rarely.

I. Inorganic Acids.

First Group.

Acids which are precipitated from Neutral Solutions by Barium Chloride.

§ 165.

For the sake of distinctness, this group is subdivided into four divisions, as follows:

a. Acids which are decomposed in acid solution by hydrogen sulphide, and to which attention has therefore been directed already in the testing for bases, viz., chromic acid (sulphurous acid, and thiosulphuric acid, the latter because it is decomposed and detected by the mere addition of hydrochloric acid, to the solution of one of its salts; and also iodic acid).*

b. Acids which are not decomposed in acid solution by hydrogen

* To this first division of the first group of inorganic acids belong properly also all the oxygen compounds of a distinctly pronounced acid character, which have been discussed already with the Sixth Group of the metals (acids of arsenic, antimony, selenium, etc.). But as the reaction of these compounds with hydrogen sulphide leads to confounding them with other metals rather than with other acids, it appears the safer course to class these compounds, which stand, to a certain degree, upon the border-line between bases and acids, with the metallic radicals.

sulphide, and the barium compounds of which are insoluble or scarcely soluble in hydrochloric acid, viz., SULPHURIC ACID (hydrofluosilicic acid).

c. Acids which are not decomposed in acid solution by hydrogen sulphide, and the barium compounds of which dissolve in hydrochloric acid, apparently without decomposition, inasmuch as the acids cannot be completely separated from the hydrochloric acid solution by heating or evaporation, viz., PHPOSHORIC ACID, BORIC ACID, OXALIC ACID, HYDROFLUORIC ACID (phosphorous acid). (Oxalic acid, although it will also be considered with the organic acids, is included here, because its salts are decomposed upon ignition, without actual carbonization, and this fact may lead to its being overlooked as an organic acid.)

d. Acids which are not decomposed in acid solution by hydrogen sulphide, and the barium salts of which are soluble in hydrochloric acid, with separation of the acid, viz., CARBONIC ACID, SILICIC ACID.

First Division of the First Group of Inorganic Acids.

§ 166.

CHROMIC ACID (*Anhydride*), CrO_3.

1. CHROMIUM TRIOXIDE forms a scarlet, crystalline mass, or distinct acicular crystals. Upon ignition, it is resolved into chromic oxide, Cr_2O_3, and oxygen. It deliquesces rapidly upon exposure to the air. It dissolves in water, imparting to the fluid a deep reddish-yellow tint, which remains visible in very dilute solutions.

2. The CHROMATES are all red or yellow, and for the most part insoluble in water. Part of them are decomposed upon ignition. Those with alkali bases are soluble in water, and when normal are not decomposed by ignition; the solutions of the normal alkali-metal chromates are yellow, those of the acid chromates are reddish-yellow. These tints are visible in highly dilute solutions. The yellow color of the solution of a normal salt changes to reddish-yellow on the addition of an acid.

3. *Hydrogen sulphide*, acting upon the acidified solution, produces first a brownish coloration of the fluid, then a green color, arising from the formation of a chromic salt. This change of color is attended with separation of sulphur, which imparts a milky appearance to the fluid: $K_2Cr_2O_7 + 4H_2SO_4 + 3H_2S = K_2SO_4 + Cr_2(SO_4)_3 + 3S + 7H_2O$. Heat promotes the reaction, part of the sulphur being in that case converted into sulphuric acid.

4. *Ammonium sulphide*, when added in excess to a solution of an alkali dichromate, immediately produces a bluish gray-green precipitate, consisting essentially of chromic hydroxide and sulphur. In a solution of normal potassium chromate, at first a dark brownish coloration alone is produced, but the bluish gray-green precipitate above mentioned soon separates. The precipitations are complete only upon boiling. After being washed, the precipitate dissolves in hydrochloric acid, giving off an odor of hydrogen persulphide.

5. Chromic acid may also be reduced to chromic oxide by means of many other substances, and more particularly by *sulphurous acid*, by heating with concentrated *hydrochloric acid*, or with the dilute acid and alcohol (in which case ethyl chloride and aldehyde are evolved); by *stannous chloride* or *metallic zinc* in the presence of hydrochloric or sulphuric acid, by heating with *tartaric acid*, *oxalic acid*, etc. All these reactions are clearly characterized by the change of the red or yellow color of the solution to the green or violet tint of the chromic salt. Alkaline solutions of chromates are not reduced by alcohol, even upon heating (difference from manganic and permanganic acids).

6. In aqueous solutions of chromates, *barium chloride* produces a yellowish-white precipitate of BARIUM CHROMATE, $BaCrO_4$, soluble in dilute hydrochloric and nitric acids. This dissolves very slightly in cold water, but somewhat more in hot water. Ammonium salts increase the solubility very noticeably, and acetic acid increases it considerably. The solubility in these weaker solvents disappears completely, however, if normal potassium or ammonium chromate is added.

7. In aqueous solutions of normal chromates, *silver nitrate* produces a dark brownish-red precipitate of SILVER CHROMATE,

Ag_2CrO_4, easily soluble in nitric acid and in ammonia. In slightly acid solutions, it produces a dark red to reddish-brown, crystalline precipitate of SILVER DICHROMATE, $Ag_2Cr_2O_7$, which dissolves easily in ammonia, and somewhat less readily in nitric acid.

8. In an aqueous or acetic acid solution of a chromate, *lead acetate* produces a yellow precipitate of LEAD CHROMATE, $PbCrO_4$; insoluble in ammonia, soluble in potassium hydroxide and sodium hydroxide solutions, sparingly soluble in dilute nitric acid, and insoluble in acetic acid. Upon heating with alkalies, the yellow normal salt is converted into a red basic chromate, $PbCrO_4.PbO$.

9. If a very dilute, acid solution of *hydrogen peroxide** (about 6 or 8 cc) is covered with a layer of ether (about half a centimeter thick), and a fluid containing chromic acid is added, the solution of hydrogen peroxide acquires a fine blue color. By closing the test-tube with the thumb, and inverting it repeatedly, without much shaking, the solution becomes colorless, while the ether acquires a blue color. The latter reaction is particularly characteristic. One part of potassium chromate in 40,000 parts of water suffices to produce it distinctly (STORER); but the presence of vanadic acid materially impairs the delicacy of the test (WERTHER).† This blue coloration is caused by perchromic acid, Cr_2O_7. After some time, it is reduced to a chromic salt, and the ether is decolorized.

10. If insoluble chromates are fused with *sodium carbonate* with the addition of some potassium chlorate, and the mass is treated with water, a solution is obtained which is colored yellow from the alkali chromate dissolved in it, and which becomes reddish-yellow upon the addition of an acid. The

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* If a solution of hydrogen peroxide is not at hand, a solution which is adapted for making the experiment may be easily prepared by triturating a fragment of barium dioxide (about the size of a pea) with some water, and adding it with stirring to a mixture of about 30 cc hydrochloric acid and 120 cc water. The solution keeps a long time without suffering decomposition. In default of barium dioxide, impure sodium dioxide may be used, which is obtained by heating a fragment of sodium in a porcelain capsule until it takes fire, and letting it burn.

† Journ. f. prakt. Chem., 83, 195.

metals of the original insoluble chromates remain undissolved as oxides or carbonates, when the mass is treated with water.

11. In the blowpipe flame, the chromates show the same reactions with *sodium metaphosphate* and with *borax* as chromic oxide compounds.

12. Very minute quantities of chromic acid may be detected in aqueous solution by one of the following methods: *a.* Mix with the fluid, slightly acidified with sulphuric acid, a little tincture of guaiacum (1 part of the resin to 100 parts of alcohol of 60 per cent), when an intense blue coloration of the fluid will at once make its appearance, speedily vanishing again, however, where mere traces of chromic acid are present (H. SCHIFF). *b.* Dissolve a little *diphenylamine* in concentrated sulphuric acid, and add a drop of the solution containing chromic acid. A distinct blue coloration shows the presence of chromic acid. *c.* Moisten a small piece of *starch* with a freshly prepared *potassium iodide* solution, and drop upon it some of the chromic acid solution which is acidified with dilute hydrochloric or sulphuric acid, or add a small amount of *carbon disulphide* to a freshly prepared *potassium iodide* solution, add the chromic acid solution acidified with hydrochloric or sulphuric acid, and shake. The occurrence of a violet coloration of the starch or of the carbon disulphide allows the detection of even the minutest traces of chromic acid. With the reactions mentioned in 12, the presence of chromic acid is shown *only* when it is certain that other substances which give the same or similar reactions (and there are many of them) are absent.

Chromic acid being reduced by hydrogen sulphide to a chromic salt, the element is always found in the course of analysis in the examination for bases. The intense color of the solutions containing chromic acid, the excellent reaction with hydrogen peroxide, and the characteristic precipitates produced by solutions of lead and of silver salts, afford, moreover, ready means for its detection. For the discovery of traces of chromium present in many minerals, for instance in serpentine, the reactions in 12 may be used after the mineral has been fused with sodium carbonate and potassium chlorate. Concerning the detection of normal alkaline chromates in the presence of

dichromates, of dichromates in the presence of normal chromates, and of free chromic acid in alkaline dichromates, compare E. DONATH, Zeitschr. f. analyt. Chem., **18**, 78. In regard to the microchemical detection of chromic acid, see § 108.

Rarer Acids of the First Division.

§ 167.

1. SULPHUROUS ACID, H_2SO_3. (*Sulphurous Anhydride*, SO_2.)

SULPHUR DIOXIDE OR SULPHUROUS ANHYDRIDE, SO_2, is a colorless, non-inflammable gas, which has the stifling odor of burning sulphur. It dissolves copiously in water. The solution has the odor of the gas, reddens litmus-paper, and bleaches Brazil-wood paper. It gradually absorbs oxygen from the air, and is thereby converted into dilute sulphuric acid. The salts are colorless. Of the normal sulphites, only those with alkali bases are readily soluble in water; while many of the sulphites insoluble or sparingly soluble in water dissolve in an aqueous solution of sulphurous acid, but fall down again on boiling. All the sulphites evolve sulphur dioxide when treated with *sulphuric acid*, and this can be readily distilled from the solutions. *Chlorine-water* changes sulphites to sulphates, and consequently dissolves most of them. *Barium chloride* precipitates normal sulphites, but not free sulphurous acid. The precipitate dissolves in hydrochloric acid. Alkali-metal acid sulphites yield, besides the precipitate of normal barium sulphite, free sulphurous acid, which remains in solution. *Hydrogen sulphide* decomposes free sulphurous acid, water and pentathionic acid being formed, with separation of sulphur. If to a solution of sulphurous acid mixed with an equal volume of hydrochloric acid, a piece of clean *copper* wire is added, and the mixture is boiled, the copper appears black, as if covered with soot, if much sulphurous acid is present; but only dull if little is present (H. REINSCH). If a trace of sulphurous acid or of a sulphite is introduced into a flask in which hydrogen is being evolved from sulphur-free *zinc* or *aluminium* and *hydrochloric acid* free from sulphurous acid, hydrogen sulphide is immediately evolved along with the hydrogen, and the gas now produces a black coloration or a black precipitate in a solution of lead acetate to which has been added a sufficient quantity of caustic soda to redissolve the precipitate which forms at first Sulphurous acid is a powerful *reducing agent*. It reduces chromic acid, permanganic acid, iodic acid, mercurous nitrate, and upon heating (in the presence of a considerable amount of alkali-metal chloride), it reduces mercuric chloride (to mercurous chloride). It decolorizes iodized starch,

and produces a blue precipitate in a mixture of potassium ferricyanide and ferric chloride, etc. If, therefore, filter-paper is wet with a dilute starch solution* containing some pure potassium iodate (A. FRANK), or with a solution of ferric chloride and potassium ferricyanide (C. BROWN), and the paper is dried, very delicate test-papers for sulphurous acid are obtained. The resulting blue colorations are *conclusive* tests for sulphurous acid *only* when other reducing agents are certainly not present. The papers, in a moistened condition, are therefore especially adapted for the detection of minute amounts of gaseous sulphurous acid. *Silver nitrate* precipitates, from a solution of sulphurous acid, white silver sulphite, soluble in nitric acid. With a hydrochloric acid solution of *stannous chloride*, a yellow precipitate of STANNIC SULPHIDE is formed after some time. If an aqueous solution of an alkali-metal sulphite is mixed, if not neutral, according to circumstances, with acetic acid to give it an exactly neutral reaction, or with hydrogen sodium carbonate (an excess of which is without disadvantage, while an excess of alkaline hydroxide, normal carbonate, or ammonium carbonate may prevent the reaction), and is then added to a relatively large amount of solution of *zinc sulphate* mixed with a very small quantity of *sodium nitroprusside*, the fluid acquires a red color if the quantity of sulphite present is not too inconsiderable. When, however, the amount of sulphite is very minute, the coloration makes its appearance only after addition of some solution of potassium ferrocyanide. If the quantities are not altogether too small, a purple-red precipitate will form upon the addition of the potassium ferrocyanide (BÖDEKER). Thiosulphates of the alkalies do not show this reaction. Concerning the microchemical detection of sulphurous acid, compare DENIGÈS, Pharmac. Centralhalle, 1892, p. 98.

§ 168.

2. THIOSULPHURIC ACID, $H_2S_2O_3$.

Thiosulphuric anhydride, S_2O_2, does not exist in the free state. Most of its salts are soluble in water. The solutions of most thiosulphates may be boiled without suffering decomposition; but upon boiling its solution, calcium thiosulphate is resolved into calcium sulphite and sulphur. The alkali-metal thiosulphates, when heated out of contact with air, decompose into water, sulphur and hydrogen sulphide, which escape, and a mixture of sulphide and sulphate of the alkali metal, which remains behind. If *sulphuric* or *hydrochloric acid* is added to the solution of a thiosulphate, the liquid at first remains clear and odorless, but after a short time (the shorter, the more concentrated and warmer the solution), it becomes more and more turbid, owing to the sep-

* 2 g of wheat starch, 100 g of water, and .2 g of potassium iodate.

aration of sulphur, and exhales the odor of sulphur dioxide. *Silver nitrate* produces a white precipitate of SILVER THIOSULPHATE, which is soluble in an excess of the thiosulphate, and after a little while (upon heating, almost immediately) turns black, being decomposed into silver sulphide and sulphuric acid. Sodium thiosulphate dissolves silver chloride; upon the addition of an acid, the solution remains clear at first, but after some time, and immediately upon boiling, silver sulphide separates. *Barium chloride* produces a white precipitate, which is soluble in much water, more especially hot water, and is decomposed by hydrochloric acid. *Ferric chloride* colors the solutions of alkali thiosulphates reddish-violet (difference from alkali sulphites); but on standing, the liquid loses its color, especially when heated, ferrous chloride being formed. Acidified solution of *chromic acid* is immediately reduced by thiosulphates to green chromic salt solutions. When the chromic acid solution is not acidified, it turns brown, and upon heating, it yields brown chromic chromate. *Iodized starch* solution and an acidified solution of *potassium permanganate* are decolorized at once. With *zinc* or *aluminium* and *hydrochloric acid* the thiosulphates behave like the sulphites. Treated with *potassium* or *sodium hydroxide* and *aluminium*, sulphides of the alkali metals are obtained (DE KONINCK, difference from sulphites).

Where it is required to find sulphites and thiosulphates of the alkali metals in presence of alkali-metal sulphides, as is often the case, solution of zinc sulphate is first added to the fluid until the sulphide is decomposed; the zinc sulphide is then filtered off, and one part of the filtrate is tested for thiosulphuric acid by addition of hydrochloric acid or with aluminium and potassium hydroxide, another portion for sulphurous acid with sodium nitroprusside, etc.

§ 169.

3. IODIC ACID, HIO_3. (*Iodic Anhydride*, I_2O_5.)

IODIC ANHYDRIDE forms a white, crystalline powder, while the acid forms colorless, rhombic crystals. Both are readily soluble in water, and are decomposed at a moderate heat into iodine vapor and oxygen, and, in the case of the hydrated acid, water also. The salts are decomposed upon ignition, being resolved either into oxygen and a metallic iodide, or into iodine, oxygen, and metallic oxide. Only the iodates of the alkali metals dissolve readily in water. From solutions of alkali-metal iodates, *barium chloride* throws down a white precipitate of barium iodate, which is soluble in nitric acid. *Silver nitrate* gives a white, granular, crystalline precipitate of silver iodate, which dissolves readily in ammonia, but only sparingly in nitric acid. *Lead acetate* precipitates white lead iodate, which is scarcely

soluble in water, and difficultly so in nitric acid. *Hydrogen sulphide* precipitates iodine from solutions of iodic acid, with the simultaneous separation of sulphur. Upon further addition of hydrogen sulphide, the iodine dissolves in the hydriodic acid formed, and with an excess of hydrogen sulphide, the liquid becomes decolorized with further separation of sulphur, while the iodine is completely converted into hydriodic acid. Iodic acid when combined with bases is also decomposed by hydrogen sulphide. *Sulphurous acid* throws down iodine, which is converted into hydriodic acid by an excess of the sulphurous acid. A boiling, saturated solution of *oxalic acid* expels all the iodine from salts of iodic acid. *Phosphorus* (colorless as well as red, the latter with especial energy) reduces free and combined iodic acid even in very dilute solutions, with the formation of phosphoric acid and the separation of iodine (POLACCI). To detect iodic acid in nitric acid, it is best to dilute the latter with about 2 volumes of water, to add a little carbon disulphide or chloroform and *one* drop of an aqueous solution of sulphurous acid, and to shake the mixture. If iodic acid was present, the carbon disulphide or chloroform is colored violet in consequence of taking up the iodine set free. An excess of sulphurous acid is, of course, to be avoided.

Second Division of the First Group of Inorganic Acids.

§ 170.

SULPHURIC ACID, H_2SO_4. (*Sulphuric Anhydride*, SO_3.)

1. SULPHUR TRIOXIDE OR SULPHURIC ANHYDRIDE, SO_3, usually forms a white, feathery, crystalline mass, which fumes strongly upon exposure to the air; while CONCENTRATED SULPHURIC ACID (which contains a little more water than the formula H_2SO_4 requires) forms an oily liquid, colorless and transparent like water. Both the anhydride and the acid char organic substances, and combine with water in all proportions, the process of combination being attended with considerable elevation of temperature, and in the case of the anhydride, with a hissing noise.

2. The normal SULPHATES are readily soluble in water, with the exception of the sulphates of barium, strontium, calcium, and lead. The basic sulphates of the heavy metals which are insoluble in water dissolve in hydrochloric or in nitric acid. Most of the sulphates are colorless or white. Those of the

alkali and alkali-earth metals are not decomposed by moderate ignition, but are more or less easily decomposed at *very* high temperatures. The other sulphates are variously acted upon by a moderate red heat, some of them being readily decomposed, and many others resisting decomposition.

3. Even in exceedingly dilute solutions of sulphuric acid and of the sulphates, *barium chloride* produces a finely pulverulent, heavy, white precipitate of BARIUM SULPHATE, $BaSO_4$, scarcely soluble in dilute hydrochloric and nitric acids. From very dilute solutions, the precipitate separates only after standing for some time. Concentrated acids and concentrated solutions of many salts impair the delicacy of the reaction, while a certain excess of barium chloride increases it.

4. *Lead acetate* produces a heavy, white precipitate of LEAD SULPHATE, $PbSO_4$, which is but slightly soluble in water, still less so in dilute sulphuric acid, insoluble in alcohol, and sparingly soluble in dilute nitric acid, but dissolves completely in hot concentrated hydrochloric acid. It is dissolved by hot solutions of ammonium tartrate or acetate.

5. The sulphates of the alkali-earth metals which are insoluble in water and acids are converted into CARBONATES by fusion with *alkali-metal carbonates;* but lead sulphate yields LEAD OXIDE when treated in this manner. In both cases, alkali-metals sulphates are formed. The sulphates of the alkali-earth metals and of lead are also resolved into insoluble carbonates and soluble alkali sulphates, by digestion or boiling with concentrated solutions of carbonates of the alkali metals. In the case of barium sulphate, however, repeated boiling with renewal of the solution is necessary for complete decomposition.

6. Upon fusing sulphates with *sodium carbonate* on *charcoal* in the inner flame of the blowpipe, or heating them in the stick of charcoal (p. 34) in the lower reducing flame, the sulphuric acid is reduced, and sodium sulphide formed, which may be readily recognized by the odor of hydrogen sulphide emitted upon moistening the sample and the part of the charcoal into which the fused mass has penetrated, and adding a small quantity of an acid. If the fused mass is transferred to a clean silver plate, or a polished silver coin, and then moistened with water, a black stain of silver sulphide is immediately produced. (Compounds

of tellurium and selenium give the same reaction.) Since the gas flame contains sulphur, these experiments by fusion should be made by the help of an alcohol-lamp.

7. Concerning the microchemical detection of sulphuric acid, see HAUSHOFER, p. 115; BEHRENS, Zeitschr, f. analyt. Chem., **30**, 166.

Remarks.—The characteristic and exceedingly delicate reaction of SULPHURIC ACID with barium salts renders the detection of this acid an easier task than that of almost any other. It is simply necessary to take care not to confound with barium sulphate, precipitates of barium chloride, and particularly of barium nitrate, which are formed upon mixing aqueous solutions of these salts with fluids containing a large proportion of free hydrochloric acid or free nitric acid. It is very easy to distinguish these precipitates from barium sulphate, since they redissolve immediately upon diluting the acid fluid with water. To dilute the fluid largely is a rule that should never be departed from in testing for sulphuric acid with barium chloride. A little hydrochloric acid should also be added, which counteracts the adverse influence of many salts—for instance, citrates of the alkali metals. Where very minute quantities of sulphuric acid are to be detected, the fluid, after the addition of a sufficient excess of barium chloride, should be allowed to stand several hours at a gentle heat. The trace of barium sulphate formed will in that case be found deposited at the bottom of the vessel. When the least uncertainty exists about the nature of the precipitate produced by barium chloride in presence of hydrochloric acid, the reaction in 6 will at once remove all doubt. In testing for very small quantities of sulphuric acid in the presence of much hydrochloric or nitric acid, the greater part of the latter should first be evaporated off or neutralized with an alkali before adding barium chloride. To detect *free sulphuric acid* in presence of a sulphate, the fluid is mixed with a very little cane-sugar, and evaporated to dryness in a porcelain dish at 100°. If free sulphuric acid was present, a black residue remains, or in the case of most minute quantities, a blackish-green residue. Other free acids do not decompose cane-sugar in this way. The reaction may be also carried out by adding a very

minute amount of cane-sugar (about .2 to .3 per cent) to the solution, and allowing the lower end of a strip of filter-paper 30 or 40 cm long to dip into it. After 24 hours, the strip of paper is dried and heated to 100°. In the presence of free sulphuric acid, the paper becomes brown or black, and often very brittle, at the upper limit of the moistened part (NESSLER).

§ 171.

HYDROFLUOSILICIC ACID, H_2SiF_6.

HYDROFLUOSILICIC ACID forms a white, deliquescent mass, which fuses at 19°, and is easily soluble in water. The aqueous solution is a very acid fluid, which volatilizes completely upon evaporation in platinum, as silicon fluoride and hydrofluoric acid. When evaporated in glass, it etches the latter. With bases, it forms water and silicofluorides, most of which are soluble in water, redden litmus-paper, and upon ignition are resolved into metallic fluorides and silicon fluoride. *Barium chloride* forms a crystalline precipitate with hydrofluosilicic acid (§ 100, 6). Strontium chloride forms no precipitate with this acid, while lead acetate added in excess gives a white precipitate. *Potassium salts* precipitate transparent, gelatinous potassium silicofluoride. *Ammonia* in excess throws down hydrated silicic acid, with formation of ammonium fluoride. By heating metallic silicofluorides with concentrated *sulphuric acid*, dense fumes are emitted in the air, arising from the evolution of hydrofluoric acid and silicon fluoride. If the experiment is conducted in a platinum vessel covered with glass, the fumes etch the glass (§ 176, 5), while the residue contains the sulphates formed.

Third Division of the First Group of Inorganic Acids.

§ 172.

a. PHOSPHORIC ACID, H_3PO_4. (*Phosphoric Anhydride*, P_2O_5.)

1. COMMON PHOSPHORUS is a colorless, transparent, solid body, of 1.83 sp. gr., with a waxy appearance. It is insoluble in water, somewhat soluble in alcohol and in ether, and easily soluble in carbon disulphide. Taken internally, it acts as a virulent poison. It fuses at 44.3°, and boils at 290°, but it volatilizes in

small amount even upon distillation with water. By the influence of light, phosphorus kept under water turns first yellow, then red, and is finally covered with a white crust. If exposed to the air at the common temperature, it exhales a highly characteristic and most disagreeable odor, copious fumes being evolved, which are luminous in the dark. These fumes are formed by oxidation of the vapor of phosphorus, and consist of phosphoric and phosphorous acids and phosphorus vapor. When the air is moist, ozone, hydrogen dioxide, and ammonium nitrite are produced at the same time. Phosphorus very readily takes fire, burning with a luminous flame to phosphoric anhydride, the greater part of which appears in the form of white fumes. By the protracted influence of light, or by heating to 250° out of contact with air, phosphorus is converted into RED (so-called amorphous) PHOSPHORUS. Red phosphorus does not alter in the air, is not luminous, its inflammability is much decreased, it is not poisonous, has a specific gravity of 2.1, and does not dissolve in carbon disulphide. Nitric acid and nitro-hydrochloric acid dissolve colorless phosphorus rather readily upon heating. Besides phosphoric acid, the solutions at first also contain phosphorous acid. Hydrochloric acid does not dissolve phosphorus. If phosphorus is boiled with solution of potassium or sodium hydroxide, or with milk of lime, hypophosphites and phosphates are formed, while spontaneously-inflammable hydrogen phosphide gas escapes. If a substance containing colorless phosphorus is placed at the bottom of a flask, and a strip of paper moistened with solution of silver nitrate is suspended inside the flask by means of a cork loosely inserted into its mouth, and a gentle heat applied (from 30° to 40°), the paper will turn black, in consequence of the reducing action of the phosphorus fumes, even though only a most minute quantity of the phosphorus is present. If, after the termination of the reaction, the blackened part of the paper is boiled with water, the undecomposed portion of the silver salt precipitated with hydrochloric acid, the fluid filtered, and the filtrate evaporated as far as practicable on the water-bath, the presence of phosphoric acid in the residue may be shown by means of the reactions described below (J. SCHERER). It must be borne in mind that the silver salt is also blackened by hydrogen sulphide,

formic acid, volatile products of putrefaction, etc., and, moreover, that the detection of phosphoric acid in the strip of paper can be of value only where the latter and the filtering-paper were perfectly free from phosphoric acid. As regards the deportment of phosphorus upon boiling with dilute sulphuric acid, and in a hydrogen evolution apparatus supplied with zinc and dilute sulphuric acid, see the detection of phosphorus, Part II, Division II.

2. ANHYDROUS PHOSPHORIC ACID, P_2O_5, is a white, snow-like mass, which rapidly deliquesces in the air. When treated with water, it hisses, and is at first only partially dissolved; in time, however, the solution is complete. With water and bases, it forms three series of compounds; viz., with 3 molecules of water or with an equivalent amount of base, orthophosphoric acid or common phosphates; with 2 molecules of water or the corresponding amount of base, pyrophosphoric acid or pyrophosphates; with 1 molecule of water or its equivalent of base, metaphosphoric acid or metaphosphates. Since compounds of orthophosphoric acid only are usually encountered in nature and in analysis, these alone will be discussed in a comprehensive manner, while pyro- and metaphosphoric acids will be treated more briefly in a supplementary paragraph.

3. ORTHOPHOSPHORIC ACID, H_3PO_4, forms colorless and pellucid crystals, which deliquesce rapidly in the air to a syrupy, non-caustic liquid. The action of heat changes it into meta- or pyrophosphoric acid, according to whether one or two molecules of water are expelled from $2H_3PO_4$. Heated in an open platinum dish, orthophosphoric acid, if pure, volatilizes completely, though with difficulty, in white fumes.

4. The action of heat fails to decompose the ORTHOPHOSPHATES with fixed bases, but converts them into pyrophosphates if they contain one hydrogen or one ammonium, and into metaphosphates if they contain two hydrogens or other volatile radicals. Of the normal orthophosphates, only those with alkali bases are soluble in water. The solutions manifest alkaline reactions. If pyro- or metaphosphates are fused with excess of sodium carbonate, the fused mass contains only orthophosphates.

5. In aqueous solutions of alkaline phosphates having a neutral or alkaline reaction, but not in those having an acid reaction (dihydrogen phosphates), *barium chloride* produces white

precipitates of BARIUM PHOSPHATE, $HBaPO_4$ or $Ba_3(PO_4)_2$,* which are soluble in hydrochloric and nitric acids, but difficultly soluble in ammonium chloride.

6. In neutral or alkaline solutions of phosphates, but not in solutions of phosphoric acid, solution of *calcium sulphate* produces a white precipitate of HYDROGEN CALCIUM PHOSPHATE, $HCaPO_4.2H_2O$, or of TRICALCIUM PHOSPHATE, $Ca_3(PO_4)_2$, which dissolves readily in acids, even in acetic acid if it is still in an amorphous condition, and in this state, it is soluble also in ammonium chloride.

7. In concentrated solutions of dimetallic alkali phosphates, *magnesium sulphate* produces a white precipitate of HYDROGEN MAGNESIUM PHOSPHATE, $HMgPO_4.7H_2O$, which often separates only after some time; but upon boiling, a precipitate of TRIMAGNESIUM PHOSPHATE, $Mg_3(PO_4)_2.7H_2O$, is thrown down immediately. The latter precipitate forms also upon addition of magnesium sulphate to the solution of a trimetallic alkali phosphate. But if a mixture of *magnesium sulphate* and sufficient ammonium chloride to keep it clear when it contains ammonia is added to a solution of phosphoric acid or of an alkali-metal phosphate, and then an excess of ammonia is also added, a white, crystalline and quickly subsiding precipitate of AMMONIUM MAGNESIUM PHOSPHATE, $NH_4MgPO_4.6H_2O$, is formed, even in highly dilute solutions. This precipitate is almost entirely insoluble in ammonia, and most sparingly soluble in ammonium chloride, but dissolves readily in acids, even in acetic acid. It makes its appearance often only after the lapse of some time, but stirring promotes its separation (§ 103, 8). The reaction can be considered decisive only if no arsenic acid is present (§ 156, 8).

8. *Silver nitrate* throws down from solutions of di- and trimetallic alkali phosphates, a light yellow precipitate of SILVER PHOSPHATE, Ag_3PO_4, which is readily soluble in nitric acid and in ammonia. If the solution contained a trimetallic phosphate, the fluid in which the precipitate is suspended manifests a neutral reaction, while the reaction is acid if the solution contained

* A precipitate corresponding to the first formula is produced when the solution contains an alkaline phosphate with one hydrogen and two alkali-metal atoms or ammoniums, while a precipitate corresponding to the second formula is formed where the phosphate is tribasic.

a dimetallic phosphate. The acid reaction in the latter case arises from the circumstance that the nitric acid radical receives only 2 atoms of alkali metal for the 3 atoms of silver which it yields to the phosphoric acid: $HK_2PO_4 + 3AgNO_3 = Ag_3PO_4 + 2KNO_3 + HNO_3$.

9. If a tolerably large amount of sodium acetate is added to a solution containing phosphoric acid and little or no free acid, and then a drop of *ferric chloride*, a yellowish-white, flocculent, gelatinous precipitate of FERRIC PHOSPHATE, $FePO_4.2H_2O$, is produced. An excess of ferric chloride must be avoided, as ferric acetate (of a red color) would thereby be formed, in which the precipitate is not insoluble. This reaction is of importance, as it enables us to detect phosphoric acid in phosphates of the alkali-earth metals; but it can be held to be decisive, only if no arsenic acid is present, as this shows a very similar reaction. To effect the complete separation of phosphoric acid from the alkali-earth metals, a sufficient quantity of ferric chloride is added to impart a reddish color to the solution, which is then boiled (whereby the whole of the iron is thrown down, partly as phosphate, partly as basic acetate), and filtered hot. The filtrate contains the alkali-earth metals as chlorides. In order to detect, by means of this reaction, phosphoric acid in presence of a large proportion of ferric salts, boil the hydrochloric acid solution with sodium sulphite until the ferric chloride is reduced to ferrous chloride, as indicated by decoloration; add sodium carbonate until the fluid is nearly neutral, then sodium acetate, and finally one drop of ferric chloride. The reason for this proceeding is that ferrous acetate does not dissolve ferric phosphate.

10. If a few cubic centimeters of the solution of *ammonium molybdate* in nitric acid (§ 55) are placed in a test-tube, and a little of a liquid containing phosphoric acid in neutral or acid solution is added, there is formed immediately or in a short time, even in the cold, if the amount of phosphoric acid is at all considerable, a pulverulent, pale yellow precipitate of AMMONIUM PHOSPHOMOLYBDATE, which gathers upon the sides and bottom of the test-tube. When the phosphoric acid is present in exceedingly minute quantity, *e.g.*, 0.00002 g, it is necessary to wait some hours and to apply a gentle heat, not to exceed 40°, before the precipitate appears. When other coloring matters

are not present, the liquid above the precipitate is colorless after the complete separation of the precipitate. More of the solution to be tested for phosphoric acid than a third, at the most, of the molybdenum solution used should never be added, and a mere yellow coloration of the liquid should not be considered as a reaction for phosphoric acid.

The yellow precipitate under consideration, ammonium phosphomolybdate, contains MOLYBDIC ACID, AMMONIUM, WATER, and a little PHOSPHORIC ACID (3 per cent). Since it is insoluble in dilute acids, only in the presence of an excess of molybdic acid, it may not form at all if an excess of phosphoric acid is added, a fact which should be well heeded. Hydrochloric acid, if present in considerable amount, interferes with or prevents the reaction. It may be readily removed by evaporation with nitric acid. Certain organic substances also (*e.g.*, tartaric acid and reducing agents) exert a disturbing influence, and consequently are to be removed, when necessary, by fusion with sodium carbonate and potassium nitrate. The precipitate is easily recognized, even in dark-colored liquids, after allowing it to settle. If the precipitate is washed with the molybdenum solution which serves to precipitate it, then dissolved in ammonia, and a mixture of magnesium sulphate, ammonium chloride, and ammonia is added, ammonium magnesium phosphate is obtained.

If one operates in the manner given above, phosphoric acid cannot be confused with any other acid; for arsenic acid gives no precipitate *in the cold* with the molydenum solution in question, although it gives one upon heating, and especially upon boiling (the fluid above this appears yellow for a considerable time); while silicic acid gives no reaction in the cold, although upon heating, it gives a strong yellow coloration but no precipitate.

11. If a finely powdered substance containing phosphoric acid (or a metallic phosphide) is intimately mixed with 5 parts of a flux consisting of 3 parts of *sodium carbonate*, 1 part of *sodium nitrate*, and 1 part of *silicic acid*, the mixture then fused in a platinum spoon or crucible, the mass boiled with water, the solution obtained decanted, ammonium carbonate added to it, the fluid boiled again, and the silicic acid which is thereby precipitated filtered off, the filtrate now holds in solution alkali phosphate,

and accordingly may be tested for phosphoric acid as directed in 7, 8, 9, or 10.

12. On igniting and pulverizing a substance containing phosphoric acid, placing it into a tube of the thickness of a straw and sealed at one end, adding a fragment of *magnesium wire* about 4 mm long (or a small piece of *sodium*), which should be covered by the sample, and then heating, a vivid incandescence is observed, and magnesium (or sodium) phosphide is formed. When the black contents of the tube are crushed and moistened with water, they exhale the characteristic odor of hydrogen phosphide (WINKELBLECH, BUNSEN).

13. *White of egg* is not precipitated by solution of orthophosphoric acid, nor by solutions of orthophosphates mixed with acetic acid.

14. In relation to the microchemical detection of phosphoric acid, see HAUSHOFER, p. 108; BEHRENS, Zeitschr. f. analyt. Chem., **30**, 165.

§ 173.

Appendix.

a. Pyrophosphoric acid, $H_4P_2O_7$. The solution of pyrophosphoric acid is converted by boiling into solution of orthophosphoric acid. The solutions of the salts bear heating without suffering decomposition; but upon boiling with a strong acid, the pyrophosphoric acid is converted into orthophosphoric acid. If the salts are fused with sodium carbonate in excess, orthophosphates are produced. Of the tetrametallic pyrophosphates, only those with alkali bases are soluble in water. The acid salts, *e.g.*, $H_2Na_2P_2O_7$, are converted by ignition into metaphosphates, *e.g.*, $NaPO_3$. *Barium chloride* fails to precipitate the free acid; but from solutions of the salts, it precipitates white BARIUM PYROPHOSPHATE, $Ba_2P_2O_7$, soluble in hydrochloric acid. *Silver nitrate* throws down from a solution of the acid, especially upon addition of an alkali, a white, earthy-looking precipitate of SILVER PYROPHOSPHATE, $Ag_4P_2O_7$, which is soluble in nitric acid and in ammonia. *Magnesium sulphate* precipitates MAGNESIUM PYROPHOSPHATE, $Mg_2P_2O_7$. The precipitate dissolves in an excess of the pyrophosphate, as well as in an excess of magnesium sulphate. Ammonia fails to precipitate it from these solutions (difference from metaphosphoric acid). Upon boiling the solution, it separates again. A concentrated solution of *luteocobaltic chloride*, added to a not too dilute solution of an alkali pyrophosphate, produces an immediate precipitation of pale reddish-yellow spangles (difference from phosphoric and metaphosphoric acids, C. D. BRAUN). *White of egg* is not precipitated by solutions of the acid, nor by solutions of the salts mixed with acetic acid. *Ammonium molybdate*, with addition

of nitric acid, fails to produce a precipitate at first, but afterwards yellow ammonium phosphomolybdate separates to the extent to which pyrophosphoric acid is converted into orthophosphoric acid.

b. Metaphosphoric acid. Five sorts of metaphosphates are known at present, and the acids, also, corresponding to most of these have been prepared. The several reactions by which these may be distinguished will not be entered upon here, but mention should be made of the fact that the metaphosphoric acids differ from the pyro- and orthophosphoric acids in this, that the solutions of the metaphosphoric acids, and the solutions of their salts after addition of acetic acid, precipitate *white of egg* at once. Those acids and salts which are precipitated by *silver nitrate* produce with that reagent a white precipitate. *Magnesium sulphate* produces no precipitate, but one forms when ammonia is also added, which dissolves in much ammonium chloride. All metaphosphates yield sodium orthophosphate upon fusion with sodium carbonate.

§ 174.

b. Boric Acid, H_3BO_3. (*Boric Anhydride*, B_2O_3.)

1. Boric anhydride forms a colorless, fixed glass, which is fusible at a red heat. The hydrate, HBO_2 [metaboric acid], forms a porous, white mass. The compound $HBO_2.H_2O$ [or H_3BO_3, orthoboric acid], crystallizes in scale-like plates. Boric acid is soluble in water and in alcohol, and upon evaporating the solutions, a large portion of it volatilizes along with the aqueous and alcoholic vapors. The solutions redden litmus-paper, and impart to turmeric-paper a faint brown-red tint, which acquires intensity upon drying. The borates are not decomposed upon ignition; and only those with alkali bases are readily soluble in water. The solutions of borates of the alkali metals are colorless, and all, even those of the acid salts, manifest an alkaline reaction.

2. In solutions of alkali-metal borates, if not too highly dilute, *barium chloride* produces white precipitates of barium borate, which are soluble in acids and ammonium salts. The formula for the precipitate when produced from solutions of normal borates is $Ba(BO_2)_2.2H_2O$, and from solutions of acid borates it is $Ba_2B_{10}O_{16}.6H_2O$ (H. Rose).

3. *Silver nitrate*, when mixed with concentrated solutions of normal alkali-metal borates, gives a white precipitate, colored somewhat yellowish from free silver oxide, of $2AgBO_2.H_2O$;

while from concentrated solutions of alkali-metal acid borates, it throws down white $Ag_6B_8O_{13}$. Dilute solutions of alkali-metal borates give with silver nitrate a brown precipitate of silver oxide (H. Rose). All these precipitates dissolve in nitric acid and in ammonia.

4. If dilute *sulphuric acid* or *hydrochloric acid* is added to highly concentrated, hot solutions of alkali borates, (ORTHO)BORIC ACID separates upon cooling, in the form of shining, crystalline scales.

5. If a solution of boric acid, or of a borate of an alkali metal or of an alkali-earth metal, is mixed with hydrochloric acid to slight, but distinct, acid reaction, and a slip of *turmeric-paper* is half dipped into it, and then dried on a watch-glass at 100°, the dipped half shows a peculiar RED tint (H. Rose).

This reaction is very delicate. Care must be taken not to confound the characteristic red coloration with the blackish-brown color which turmeric-paper acquires when moistened with rather concentrated hydrochloric acid and then dried, nor with the brownish-red coloration which ferric chloride, or a hydrochloric acid solution of ammonium molybdate or of zirconia gives to turmeric-paper, more particularly upon drying. By moistening turmeric-paper, reddened by boric acid, with a solution of an *alkali* or an *alkali carbonate*, the color is changed to bluish-black or greenish-black; but a little hydrochloric acid will at once restore the brownish-red color (A. Vogel, H. Ludwig).

6. If *alcohol* is poured over free boric acid or a borate—with addition, in the latter case, of concentrated sulphuric acid to liberate the boric acid,—and the alcohol is kindled, the flame appears of a very distinct YELLOWISH-GREEN color, especially upon stirring the mixture. This tint is imparted to the flame by the boric acid separated from the boric ether which volatilizes with the alcohol. The delicacy of this reaction may be considerably heightened by heating the dish which contains the alcoholic mixture, kindling the alcohol, allowing it to burn for a short time, then blowing out the flame, and afterwards rekindling it. At the first flickering of the flame, its borders will now appear green, even though the quantity of the boric acid be so minute that it fails to produce a perceptible coloring of the

flame when treated in the usual manner. *Concentrated sulphuric acid in not too small amount should be used.* As salts of copper likewise impart a green tint to the flame of alcohol, any copper which may be present must first be removed by means of hydrogen sulphide. Presence of metallic chlorides may also lead to mistakes, as the ethyl chloride formed in that case colors the borders of the flame bluish-green.

7. For the following very characteristic reaction for boric acid, a short, wide test-tube is required, which is provided with a doubly perforated stopper: Into the two holes, glass tubes bent at right angles are inserted, one of which reaches almost to the bottom of the test-tube, while the end of the other is just below the stopper. The limb of the latter tube, projecting about 5 cm, is contracted at the end to about 1 mm. If a small amount of a substance containing boric acid is placed in the test-tube, a little concentrated sulphuric acid added, and, after cooling, some methyl alcohol is gradually added, then pure hydrogen is conducted through the small apparatus, and this is kindled when the atmospheric air has been expelled, it burns green on account of containing methyl boric ether, $B(OCH_3)_3$, and the flame gives the characteristic boric acid spectrum, when it is examined with the spectroscope (see 10, Rosenbladt). If the escaping gas is led through a little potassium hydroxide free from silicic acid, this is treated in a platinum dish with hydrofluoric acid, and evaporated to dryness on the water-bath, potassium borofluoride, $KF.BF_3$, is formed, which remains undissolved upon treating the residue with 1 part of potassium acetate in 4 parts of water.

8. If a substance containing boric acid, reduced to a fine powder, is mixed, with addition of a drop of water, with 3 parts of a flux composed of $4\frac{1}{2}$ parts of *potassium disulphate* and 1 part of finely pulverized *calcium fluoride*, free from boric acid, and the paste is exposed on the loop of a platinum wire in the outer mantle of the Bunsen gas flame, or at the apex of the inner flame of the blowpipe, boron fluoride, BF_3, escapes, which imparts a green tint to the flame, though only for an instant (Turner). With readily decomposed compounds, the reaction may be obtained by simply moistening the sample with hydrofluosilicic acid, and holding it in the flame. The delicacy of the

test may be increased by mixing the substance intimately with silicic acid and fluor-spar, and heating it with concentrated sulphuric acid in a test-tube, with the addition of a fragment of marble, and conducting the escaping gases by means of a glass tube bent at a right angle and provided with a platinum blowpipe tip, into a non-luminous BUNSEN flame (KÄMMERER).

9. If a dry substance containing boric acid is heated with a half or an equal volume of *ammonium silicofluoride* * in a glass tube closed at one end, at last to redness, a sublimate of AMMONIUM BOROFLUORIDE is obtained, which, when brought into a colorless flame, colors the latter green, and when dissolved in water gives the reaction, with turmeric-paper, mentioned in 5. If the substance to be tested contains a free acid, this is to be slightly more than neutralized with sodium carbonate (STOLBA).

10. When placed in the flame of the *spectrum apparatus*, boric acid or borates, fused with sodium carbonate on the loop of a platinum wire, give (even with very small amounts of boric acid) a spectrum of four well-marked lines of equal width, equidistant from each other. B_1 is brilliant yellowish-green (coinciding with Ba γ); B_2 is brilliant light green (coinciding with Ba β); B_3 is pale bluish-green (nearly coinciding with the blue barium line); B_4 is blue, very pale, close to Sr δ (SIMMLER). Also, if a finely pulverized substance containing boric acid is rubbed up with glycerine to a thickish paste, and is brought into the flame of a BUNSEN burner with the loop of a platinum wire, a green flame is obtained which is very well adapted for spectroscopic testing (M. W. ILES).

11. In relation to the microchemical detection of boric acid, see HAUSHOFER, p. 30; BEHRENS, Zeitschr. f. analyt Chem., **30**, 159.

§ 175.

c. OXALIC ACID, $H_2C_2O_4$.

1. OXALIC ACID is a white powder, while the CRYSTALLIZED ACID, $C_2H_2O_4 + 2H_2O$, forms colorless, rhombic prisms. Both dissolve readily in water and in alcohol. By heating rapidly in open

* To be obtained by carefully neutralizing hydrofluosilicic acid with ammonia, and evaporating the filtrate in a platinum dish.

vessels, part of the acid undergoes decomposition, while another portion volatilizes unaltered. The fumes are very irritating, and provoke coughing. If the acid is heated in a test-tube, some of it sublimes unaltered.

2. The OXALATES all undergo decomposition at a red heat, the acid decomposing into carbon monoxide and carbon dioxide. The oxalates of the alkali metals, and of barium, strontium, and calcium, are converted into carbonates in this process (if pure, and if the heating takes place slowly, almost without separation of charcoal). Magnesium oxalate is converted into magnesia even by a very gentle red heat. The other metallic oxalates leave either the pure metal or an oxide behind, according to the reducibility of the metallic oxide. The alkali-metal oxalates and some others are soluble in water.

3. *Barium chloride* produces in neutral solutions of alkali oxalates, a white precipitate of BARIUM OXALATE, $BaC_2O_4.H_2O$, which dissolves very sparingly in water, more readily in water containing ammonium chloride, acetic acid, or oxalic acid, and freely in nitric acid and in hydrochloric acid. Ammonia precipitates it unaltered from the latter solutions.

4. *Silver nitrate* produces in aqueous solutions of oxalic acid and of alkali oxalates, a white precipitate of SILVER OXALATE, $Ag_2C_2O_4$, which is very slightly soluble in water, difficultly soluble in dilute nitric acid, and readily soluble in concentrated, hot nitric acid and also in ammonia.

5. *Lime-water* and all the soluble *calcium salts*, including *solution of calcium sulphate*, produce in even highly dilute aqueous solutions of oxalic acid, or of oxalates of the alkalies, white, finely pulverulent precipitates of CALCIUM OXALATE, $CaC_2O_4.H_2O$, and sometimes $CaC_2O_4.3H_2O$, which dissolve readily in hydrochloric acid and in nitric acid, but are nearly insoluble in oxalic acid and in acetic acid, and practically insoluble in water. The presence of ammonium salts does not interfere in any way with the formation of these precipitates. Addition of ammonia considerably promotes the precipitation of free oxalic acid by calcium salts. In *highly* dilute solutions, the precipitate is formed only after some time, but more quickly by heating.

6. If oxalic acid or an oxalate, in the dry state, is heated with an excess of *concentrated sulphuric acid*, the latter removes

the water necessary for the existence of the oxalic acid, and it is decomposed into CARBON MONOXIDE and CARBON DIOXIDE, the two gases escaping with effervescence: $H_2C_2O_4 = CO + CO_2 + H_2O$. If the quantity operated upon is not too minute, the carbon monoxide may be kindled, and burns with a blue flame. Should the sulphuric acid acquire a dark color in the reaction, this is a proof that the oxalic acid contained some organic substance as an admixture.

7. If oxalic acid or an oxalate is mixed with finely pulverized *manganese dioxide* (which must be free from carbonates), and a little water and a few drops of sulphuric acid are added, a lively effervescence ensues, caused by escaping CARBON DIOXIDE: $H_2C_2O_4 + MnO_2 + H_2SO_4 = 2CO_2 + 2H_2O + MnSO_4$. Free oxalic acid gives this reaction without the addition of sulphuric acid, but with less delicacy.

8. If a small quantity of a solution of oxalic acid is added to a solution of *ferrous phosphate in phosphoric acid*, the liquid assumes a DARK WINE-YELLOW coloration. The delicacy of the reaction is heightened by gentle warming (GUNN).

9. If oxalates of alkali-earth metals are boiled with a concentrated solution of *sodium carbonate*, and filtered, sodium oxalate is obtained in the filtrate, while the precipitate contains the base as carbonate. With oxalates of heavy metals, this operation is not always sure to attain the desired object, as many of these oxalates (*e.g.*, nickel oxalate) will partially dissolve in the alkaline fluid, with formation of double salts. Metals of this kind should therefore be separated as sulphides.

10. In relation to the detection of oxalic acid or calcium oxalate by means of the microscope, compare C. BISCHOFF, Zeitschr. f. analyt. Chem., **22**, 633; HAUSHOFER, p. 81.

§ 176.

d. HYDROFLUORIC ACID, HF.

1. Anhydrous HYDROFLUORIC ACID is a colorless, corrosive liquid, which fumes in the air, boils at 19.4°, and is readily dissolved by water. Aqueous hydrofluoric acid is distinguished from all other acids by the property of dissolving silicic oxide,

and also of dissolving or decomposing the silicates which are insoluble in hydrochloric acid. Hydrofluosilicic acid and water are formed in the process of dissolving silicic acid: $SiO_2 + 6HF = H_2SiF_6 + 2H_2O$. With metallic oxides and hydroxides, hydrofluoric acid forms metallic fluorides and water.

2. The normal FLUORIDES of the alkali metals are soluble in water (lithium fluoride is very difficultly soluble), and the solutions have an alkaline reaction. The fluorides of the alkali-earth metals are either insoluble or very difficultly soluble in water. Aluminium fluoride is not soluble. Many of the fluorides of the heavy metals are very sparingly soluble in water, as the fluorides of copper, lead, and zinc, while others dissolve in water without difficulty, as nickelous and cobaltous fluorides, silver fluoride, antimony fluoride, and stannous fluoride. Many of the fluorides insoluble or difficultly soluble in water dissolve in hydrofluoric acid, while others do not. Most of the normal fluorides bear ignition in a crucible without suffering decomposition.

3. *Barium chloride* precipitates aqueous solutions of hydrofluoric acid, but much more completely solutions of fluorides of the alkali metals. The bulky, white precipitate of BARIUM FLUORIDE, BaF_2, is almost absolutely insoluble in water, but dissolves in large quantities of hydrochloric acid or nitric acid, from which solutions, ammonia fails to precipitate it, or throws it down only very incompletely, owing to the dissolving action of the ammonium salts.

4. *Calcium chloride* produces in aqueous solutions of hydrofluoric acid or of fluorides, a gelatinous precipitate of CALCIUM FLUORIDE, CaF_2, which is so transparent as at first to induce the belief that the fluid has remained perfectly clear. Addition of ammonia promotes the complete separation of the precipitate. The latter is practically insoluble in water, and only very slightly soluble in hydrochloric acid and nitric acid in the cold; but it dissolves somewhat more readily upon boiling with hydrochloric acid. Ammonia produces no precipitate in the solution, or only a very trifling one, as the ammonium salt formed retains it in solution. Calcium fluoride is scarcely more soluble in hydrofluoric acid than in water. It is insoluble in alkaline fluids.

5. If a finely pulverized fluoride, whether soluble or insol-

uble in water, is treated in a platinum crucible with just enough *concentrated sulphuric acid* to make it into a thin paste (not with more), the crucible covered with the convex face of a watch-glass of hard glass coated with beeswax in which lines have been traced with a pointed piece of wood, the hollow of the glass filled with water, and the crucible gently heated for the space of half an hour or an hour, the exposed lines, upon the removal of the wax, will be found more or less deeply ETCHED into the glass. (The coating is made by heating the glass cautiously, putting a small piece of wax upon the convex face, and spreading the wax equally as it melts. It is removed by heating the glass gently, and wiping with a cloth.) If the quantity of hydrofluoric acid disengaged by the sulphuric acid was very minute, the etching is often invisible upon the removal of the wax; but in such cases, it will appear when the glass is breathed upon. This appearance of the etched lines is owing to the unequal capacity of condensing water which the etched and the untouched parts of the plate respectively possess. The impressions which thus appear upon breathing on the glass may, however, owe their origin to other causes; therefore, though their non-appearance may be held as a proof of the absence of fluorine, their appearance is not a positive proof of the presence of that element. At all events, they ought to be considered of value only where they can be developed again after the glass has been properly washed with water, dried, and wiped.*

This reaction fails if there is too much silicic oxide present, or if the substance is not decomposed by sulphuric acid. In such cases, one of the two following methods is resorted to, according to circumstances:

6. If a substance containing fluorine, which is decomposable by *concentrated sulphuric acid*, is heated in a finely pulverized

* J. NICKLÈS states that etchings on glass may be obtained with all kinds of sulphuric acid, and, in fact, with all acids suited to effect evolution of hydrofluoric acid. I have tried watch-glasses of Bohemian glass with sulphuric and other acids, but could get no etchings in confirmation of this statement. Still, proper caution demands that before using the sulphuric acid, it should first be positively ascertained that its fumes will not etch glass. Should the sulphuric acid contain hydrofluoric acid, the latter may be easily removed by diluting with an equal volume of water, and evaporating in a platinum dish to the original strength.

condition with that acid (directly in case it is rich in silicic acid, but with the addition of finely divided *silicic oxide* if it contains little or none of the latter substance), SILICON FLUORIDE GAS is evolved, which forms thick, white fumes in moist air, and separates silicic acid when brought in contact with water or ammonia. If the gas is led into water through a bent tube moistened inside, the latter at once has its transparency impaired, owing to the separation of silicic acid. If the quantity operated upon is rather considerable, silicic acid separates in the water, and the fluid is rendered acid by hydrofluosilicic acid (compare § 32). This process is best applied for the detection of small quantities of fluorine as follows: Heat the substance with concentrated sulphuric acid to about 160° in a small flask closed with a cork with double perforation, bearing two tubes, one of which reaches to the bottom of the flask, while the other terminates immediately under the cork. Conduct through the longer tube a slow stream of dry air into the flask, and conduct this, upon its issuing through the other tube, into a small U-shaped tube enlarged to a small bulb at the bend and containing a few drops of water. The other end of the U-tube is connected with an aspirator. The silicon fluoride which escapes with the air gives a separation of silicic acid where it comes in contact with the water; and with the described arrangement of the apparatus, even very small amounts may be distinctly recognized. For more difficultly decomposable substances, potassium disulphate is used instead of sulphuric acid, and the mixture, to which some marble is added (to insure a continuous slight evolution of gas), is heated to fusion, and kept in that state for some time in a tube of difficultly fusible glass, which is closed at one end, and provided with a gas delivery-tube at the other end. The silicon fluoride evolved in the first operation described above may also be conducted in a very slow stream into a test-tube which contains about .3 g of aniline dissolved in 15 cc of ether and 15 cc of alcohol. If fluorine is present, there is formed a white, glistening sediment of aniline silicofluoride. If this is suspended in the liquid, and a few drops of a moderately concentrated solution of sodium hydroxide in absolute alcohol are added, sodium silicofluoride gradually settles to the bottom of the tube (W. KNOP).

7. If silicates which are not decomposable by sulphuric acid are to be tested for fluorine, it is first necessary to decompose them. This is accomplished by fusing them with 4 parts of sodium and potassium carbonates. The mass is then extracted with water, the liquid is filtered, concentrated by evaporation, cooled, transferred to a platinum vessel, hydrochloric acid added to feebly acid reaction, and the fluid allowed to stand until the carbon dioxide has escaped. It is then supersaturated with ammonia, heated, filtered into a bottle, calcium chloride added to the still hot fluid, the bottle is closed, and allowed to stand. If a precipitate separates after some time, it is collected on a filter, dried, and examined by the method described in 5 or 6 (H. Rose). The foregoing method may be also used for other substances containing fluorides (*e.g.*, phosphates containing calcium fluoride), if silica is added to them; but without this addition, calcium fluoride is only very incompletely decomposed by fusion with alkali carbonates.

8. Minute quantities of fluorides in minerals, slags, etc., may also be readily detected by means of the *blowpipe*. Bend a piece of platinum foil, and insert it in a glass tube, as shown in Fig. 43; introduce the finely triturated substance mixed with sodium metaphosphate which has been fused upon charcoal and powdered, and let the blowpipe flame play upon it so that the products of combustion may pass into the tube. A fluoride treated in this way yields hydrofluoric acid gas, which betrays its presence by its pungent odor, the dimming of the glass tube (which becomes perceptible only after cleaning and drying), and the yellow tint which the acid air issuing from the tube imparts to a moist strip of Brazil-wood paper * (Berzelius, Smithson). When silicates containing metallic fluorides are treated in this manner, gaseous silicon fluoride is formed, which also colors yellow a moist strip of Brazil-wood paper inserted in the tube, and causes silicic acid to be deposited within the tube. After washing and drying the tube, it appears here and there dimmed. A small quantity of a fluoride present in a mineral containing

Fig. 43.

* Prepared by moistening strips of fine printing-paper with a decoction of Brazil-wood.

water may generally be detected by heating the substance by itself in a glass tube sealed at one end, and inserting a slip of Brazil-wood paper in the tube; under these circumstances, the paper will usually turn yellow (BERZELIUS).

9. Concerning the microchemical detection of fluorine, see HAUSHOFER, p. 50; BEHRENS, Zeitschr. f. analyt. Chem., **30**, 172.

§ 177.

Recapitulation and Remarks.—The barium compounds of the acids of the third division of the first group are dissolved by hydrochloric acid, apparently without decomposition; and alkalies therefore reprecipitate them unaltered by neutralizing the hydrochloric acid. The barium compounds of the acids of the first division show, however, the same deportment; and these acids, therefore, if present, must be removed before any conclusion regarding the presence of phosphoric acid, boric acid, oxalic acid, or hydrofluoric acid, can be drawn from the reprecipitation of a barium salt by alkalies. But leaving this point out of the question, no great value is to be placed on this reaction, not even so far as the simple detection of these acids is concerned, and far less as regards their separation from other acids, since ammonia fails to reprecipitate from hydrochloric acid solutions their barium salts (more particularly barium borate and barium fluoride), if the solution contains any considerable proportion of free acid or of an ammonium salt. *Boric acid* is very well characterized by the coloration which it imparts, either directly, or as boron fluoride or boric ether to the alcohol flame, the hydrogen flame, or the non-luminous gas flame, and also by its action on turmeric-paper. The latter reaction is more particularly suited for the detection of very minute traces. It is to be observed, however, that this reaction does not take place in the presence of nitrous acid. If oxides of the heavy metals are present, either a sublimate of ammonium borofluoride is first obtained according to § 174, 9, or the metals interfering with the reaction are first removed by hydrogen sulphide or ammonium sulphide. Before proceeding to concentrate dilute solutions of boric acid, the latter

must be combined with an alkali, otherwise a large portion of the boric acid will volatilize with the aqueous vapors. Small quantities of boric acid may also be safely and easily detected by the spectroscope.

The detection of *phosphoric acid* in compounds soluble in water is not difficult, the reaction with magnesium sulphate, etc., being well adapted for the purpose. The detection of phosphoric acid in compounds insoluble in water cannot be effected by means of magnesium solution. Ferric chloride (§ 172, 9) is well suited for the detection of phosphoric acid in its salts with the alkali-earth metals, and more particularly for the separation of the acid from these metals. The nitric acid solution of ammonium molybdate is more especially adapted to effect the detection of phosphoric acid in presence of aluminium and iron, and in general for the detection of *small* amounts of phosphoric acid. It must be again stated that both these reactions demand the *strictest* attention to the directions given. If present in combination with oxides of the fourth, fifth, or sixth group, phosphoric acid may be separated by the method given § 172, 11, or it may be simply isolated or combined with ammonium by precipitating the bases with hydrogen sulphide or ammonium sulphide.

Oxalic acid may always be easily detected in aqueous solutions of oxalates of the alkalies by solution of calcium sulphate. The formation of a finely pulverulent precipitate, insoluble in acetic acid, leaves hardly a doubt as to its presence, as racemic acid, which occurs very rarely, alone gives the same reaction. In case of doubt, the calcium oxalate may be readily distinguished from the racemate, by simple ignition with exclusion of air, as the decomposed racemate leaves a considerable proportion of charcoal behind, and, moreover, the racemate dissolves in cold solution of potassium or sodium hydroxide, in which calcium oxalate is insoluble. The deportment of the oxalates with sulphuric acid, or with manganese dioxide and sulphuric acid, also affords sufficient means to confirm the results of other tests. In insoluble salts, the oxalic acid is detected most safely by decomposing them by boiling with solution of sodium carbonate, or by hydrogen sulphide or ammonium sulphide (§ 175, 9). Attention should also be called here to the fact that there are

certain soluble oxalates which are not precipitated by calcium salts, more particularly chromic and ferric oxalates. Their non-precipitation is due to the fact that these salts form soluble double salts with calcium oxalate.

Hydrofluoric acid is readily detected in salts decomposable by sulphuric acid; only it must be borne in mind that too large a proportion of sulphuric acid impedes the free evolution of hydrofluoric gas, and thus impairs the delicacy of the reaction; also that the glass cannot be distinctly etched if, instead of hydrofluoric acid, silicon fluoride alone is evolved. Therefore, in the case of compounds abounding in silica, the safer way is to try, besides, the reaction given in § 176, 5, as well as the one given in 6. In silicates which are not decomposed by sulphuric acid, the presence of fluorine is often overlooked, because the analyst omits to examine the compound carefully by the method given in § 176, 7.

§ 178.

Phosphorous Acid, H_3PO_3. (*Phosphorous Anhydride*, P_2O_3.)

Phosphorous oxide, P_2O_3, is a white powder, which admits of sublimation, and burns when heated in the air. With a small proportion of water, it forms a thickish fluid, which by long standing yields crystals. Heat decomposes phosphorous acid into phosphoric acid and hydrogen phosphide gas which does not take fire spontaneously. It dissolves freely in water, and is poisonous. Of the salts, those with alkali bases are readily soluble in water, all the others being sparingly soluble, and dissolving in dilute acids. All the salts are decomposed by ignition into phosphates, which are left behind, and hydrogen, or a mixture of hydrogen and hydrogen phosphide, which escapes. With *silver nitrate*, separation of metallic silver takes place, more especially upon addition of ammonia and application of heat; and with *mercurous nitrate*, under the same circumstances, there is a separation of metallic mercury. From *mercuric chloride* in excess, phosphorous acid throws down mercurous chloride after some time, but more rapidly upon heating. *Barium chloride* and *calcium chloride* produce in not too dilute solutions of phosphorous acid, upon addition of ammonia, white precipitates soluble in acetic acid. A mixture of magnesium sulphate, ammonium chloride, and ammonia, precipitates only rather concentrated solutions. *Lead acetate* throws down white lead phosphite, insoluble in acetic acid. By heating to boiling with *sulphurous acid* in excess, phosphoric acid is formed, attended by separation of sulphur.

In contact with *zinc* and *dilute sulphuric acid*, phosphorous acid gives a mixture of hydrogen with hydrogen phosphide, which accordingly fumes in the air, burns with an emerald-green color, and precipitates silver and silver phosphide from solution of silver nitrate. Nitric acid interferes with the formation of hydrogen phosphide. If this is present only in small quantity, a little ferrous chloride is first added, and finally, after some time, the zinc is added. The gas containing hydrogen phosphide may be allowed to act upon pure filter-paper soaked with silver nitrate solution, or upon parchment-paper moistened with this solution, instead of using the silver nitrate solution directly (H. HAGER). If the amount of phosphorous acid is minute, the silver paper is blackened only after some hours. It should be remembered that blackening of the paper is also caused by hydrogen sulphide and hydrogen arsenide.

Fourth Division of the First Group of Inorganic Acids.

§ 179.

a. CARBONIC ACID, H_2CO_3. (*Carbon Dioxide*, CO_2.)

1. CARBON is a solid, tasteless, and odorless body, and only the very highest degrees of heat can effect its fusion and volatilization (DESPRETZ). All carbon is combustible, and yields carbon dioxide when burnt with a sufficient supply of oxygen or atmospheric air. In the diamond, carbon is crystallized, transparent, pellucid, exceedingly hard, difficultly combustible; while in the form of graphite, it is opaque, grayish-black, soft, greasy to the touch, difficultly combustible, and stains the fingers; and as charcoal, produced by the decomposition of organic matter, it is black, opaque, non-crystalline, sometimes dense, shining, and difficultly combustible, but often porous, dull, and readily combustible.

2. CARBON DIOXIDE, CARBONIC ANHYDRIDE, OR CARBONIC ACID, CO_2, at the common temperature and common atmospheric pressure, is a colorless gas of far higher specific gravity than atmospheric air, so that it may be poured from one vessel into another. It has a faint odor, a sourish taste, and reddens moist litmus-paper; but the red tint disappears again upon drying. Carbon dioxide is readily absorbed by solution of potassium hydroxide, forming a carbonate; and it dissolves rather copiously in water.

3. The AQUEOUS SOLUTION OF CARBONIC ACID has a feebly acid and pungent taste. It transiently imparts a red tint to litmus-paper, and colors solution of litmus wine-red; but it loses carbon dioxide when shaken with air in a half-filled bottle, and more completely still upon application of heat. Some of the CARBONATES lose carbon dioxide by ignition; and all of them are white or colorless in cases where their metals usually give colorless salts. Of the normal carbonates, only those with alkali bases are soluble in water. The solutions manifest a very strong alkaline reaction. The acid carbonates of the alkali and alkali-earth metals as well as those of some other metals dissolve in water.

4. The carbonates are decomposed by all free *acids* soluble in water, with the exception of hydrocyanic acid. Most of them are decomposed by acids even in the cold, but several (magnesite, for instance) require heat. The decomposition is attended with EFFERVESCENCE, carbon dioxide being disengaged as a colorless and scarcely odorous gas, which transiently imparts a reddish tint to moist litmus-paper. It is necessary to apply the decomposing acid in excess, especially when operating upon carbonates with alkali bases, since the formation of acid carbonates will frequently prevent effervescence if too little of the decomposing acid is added. Substances which it is intended to test for carbonic acid in this way should first be heated with a little water, to prevent any mistake which might arise from the escape of air bubbles upon treating the dry substances with the acid. Where there is reason to apprehend loss of carbonic acid upon boiling with water, lime-water should be used instead of pure water. If it is wished to prove that the escaping gas is really carbon dioxide, pass it into lime-water or baryta-water, or dip a glass rod in baryta-water and hold it inside the test-tube near the fluid. If the gas is carbon dioxide, the lime- or baryta-water becomes turbid (see 5).*

5. Solutions of *calcium and barium hydroxides* (lime- and baryta-water) brought into contact with carbonic acid, or with soluble carbonates, produce white precipitates of normal CALCIUM

* The delicacy of the reaction may be increased by the use of the apparatus described by O. RÖSSLER (Ber. der. deutsch. chem. Gesellsch., 1887, p. 2630), although I prefer to use the apparatus described in 5 when it is desired to detect very small amounts of carbonic acid.

CARBONATE, $CaCO_3$, or BARIUM CARBONATE, $BaCO_3$. In testing for free carbonic acid, the reagents ought always to be added in excess, as the acid carbonates of the alkali earths are soluble in water. The precipitates when separated from the liquids dissolve in acids with effervescence, and the resulting solutions, after the complete expulsion of the carbon dioxide by boiling, give no precipitates with ammonia. For the detection of exceedingly minute traces of carbonic acid, the apparatus shown in Fig. 44 is recommended, which scarcely needs a detailed description. The

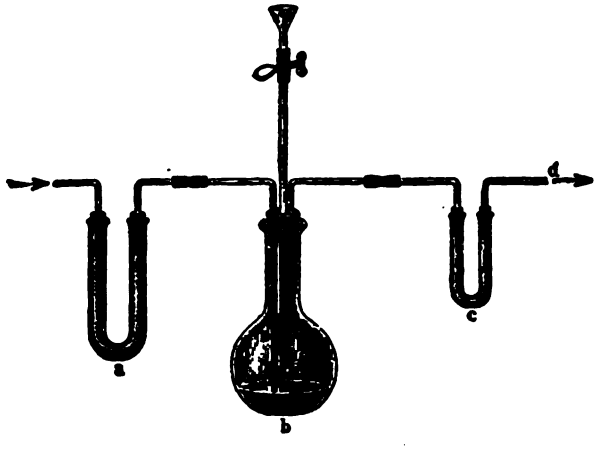

FIG. 44.

tube *a* contains soda-lime. The substance to be tested is placed in rather large amount in *b*, together with a little water, while *c* is empty at first. By suction applied at *d* by means of a jet-pump or an aspirator, the apparatus is now filled with air free from carbonic acid, then a little lime-water or baryta-water is placed in *c*, and a little hydrochloric acid is allowed to flow in through the funnel-tube, while a slow current of air freed from carbonic acid is allowed to flow through the apparatus, and *b* is gently warmed. Since lime-water dissolves a very small amount of calcium carbonate, it is advisable to saturate this by long digestion therewith (WELTER, BERTHOLLET).

6. In solutions of normal alkali carbonates, *calcium chloride* and *barium chloride* immediately produce precipitates of CALCIUM CARBONATE or of BARIUM CARBONATE; but in dilute solutions of acid carbonates, these precipitates are formed only upon

ebullition; while with aqueous carbonic acid, these reagents give no precipitate.

7. In aqueous solutions of normal and acid carbonates of the alkalies and alkali-earths, even when very dilute, an aqueous solution of *lead chloride* produces a milky, white precipitate of LEAD CARBONATE (H. SCHULZE). Free carbonic acid does not interfere with nor prevent the reaction. Acetic acid dissolves the precipitate (difference from lead sulphate).

8. For the detection of free carbonic acid in the presence of acid carbonates, a solution of 1 part of rosolic acid in 500 parts of 80 per cent alcohol, which has been treated with barium hydroxide solution until it begins to show a red coloration, may be used. For example, in testing a well-water, if there is added about .5 cc of the rosolic acid solution to 50 cc of the water, there is obtained, if the water contains free carbonic acid, a colorless, or at the most a faint yellowish, liquid; but if it contains no free carbonic acid, but only acid carbonates, the liquid becomes red (M. v. PETTENKOFER).

9. The detection of free carbonic acid, or that which is combined with normal carbonates to form acid carbonates, in the presence of normal carbonates, may be accomplished by use of the fact that NESSLER'S ammonia reaction (§ 97) does not take place when free carbonic acid or acid carbonates are present (compare SALZER, Zeitschr. f. analyt. Chem., **20**, 227.)

10. In relation to the microchemical detection of carbonic acid, see HAUSHOFER, p. 66; BEHRENS, Zeitschr. f. analyt. Chem., **30**, 158.

§ 180.

b. SILICIC ACID, H_4SiO_4, H_2SiO_3, etc. (*Anhydride*, SiO_2.)

1. SILICIC OXIDE OR SILICA is colorless or white, and in the common blowpipe flame it is unalterable and infusible. It fuses in the flame of the oxyhydrogen blowpipe, and is volatile at a very high temperature (E. CRAMER, H. MOISSAN). It is met with in both the crystalline and amorphous states. It is insoluble in water and acids (with the exception of hydrofluoric acid, which dissolves the amorphous variety easily, but the crystalline varieties

with more difficulty). Hydrated silicic acid dissolves in acids, but only at the moment of its liberation. Amorphous silicic oxide and hydrated silicic acid dissolve in hot, aqueous solutions of potassium and sodium hydroxides and their carbonates; but crystallized silica is insoluble or nearly so in these liquids. If any one of them is fused with excess of a caustic alkali or alkali carbonate, a basic alkali silicate is obtained, which is soluble in water. Aqueous ammonia dissolves gelatinous silicic acid rather readily, the dry hydrate or the amorphous anhydride more difficultly, and crystallized silica very little. The SILICATES with alkali bases are the only ones soluble in water.

2. The solutions of the alkali silicates are decomposed by all *acids*. If a large proportion of hydrochloric acid is added at once, even to concentrated solutions of alkali silicates, the liberated silicic acid remains in solution; but if the hydrochloric acid is added gradually, drop by drop, while the fluid is stirred, the greater part of the silicic acid separates in a gelatinous form. The more dilute the fluid, the more silicic acid remains in solution, and in highly dilute solutions, no precipitate is formed. If the solution of an alkali silicate, mixed with hydrochloric or nitric acid in excess, *is evaporated to dryness*, silicic acid separates as the acid escapes. Upon treating the residue with hydrochloric acid and water, silicic anhydride or, if it has been dried at only 100°, hydrated silicic acid remains as an insoluble, white powder. In not too dilute solutions of alkali silicates, ammonium chloride produces precipitates of silicic acid (containing alkali), and heating promotes the separation.

3. Some of the silicates insoluble in water are decomposed by hydrochloric or nitric acid, while others are attacked scarcely or not at all by these acids, even upon boiling. In the decomposition of the former, the greater portion of the silicic acid separates, usually in the gelatinous, more rarely in the pulverulent, form. To effect the complete separation of the silicic acid, the hydrochloric acid solution, with the precipitated silicic acid suspended in it, is evaporated to dryness, the residue is heated with stirring, at a uniform temperature, somewhat above the boiling-point of water until acid vapors no longer escape, then it is moistened with hydrochloric acid, heated with water, and the fluid containing the bases filtered from the residuary, insoluble

silicic acid. Of the silicates not decomposed by hydrochloric acid, many (*e.g.*, kaolin) are completely decomposed by heating with a mixture of 8 parts of strong sulphuric acid and 3 parts of water, the silicic acid being separated in the pulverulent form; many others are acted upon to some extent by this reagent. Silicates not decomposable by boiling with hydrochloric or sulphuric acid in the open air (at the ordinary atmospheric pressure) may generally be completely decomposed by heating, in a state of fine powder, with the acids, in strong, sealed glass tubes at 200°–210° in an air- or paraffin-bath.

4. If any silicate, reduced to a fine powder, is fused with 4 parts of *sodium and potassium carbonates* until no more carbon dioxide escapes, and the mass is then boiled with water, the greater part of the silicic acid dissolves as alkali-metal silicate, while alkali-earth and earth metals (with the exception of aluminium, which passes more or less completely into the solution) and heavy metals are left undissolved as carbonates or oxides. If the fused mass is softened with water, then, without previous filtration, hydrochloric or nitric acid added to strongly acid reaction, and the fluid evaporated as directed in 3, the silicic acid is left undissolved, while the bases are in solution. If a fusion is made with 4 parts of *barium hydroxide*, the mass is digested with water with the addition of hydrochloric or nitric acid, and the acid solution is treated according to 3, silicic acid is separated as before. The bases, especially the alkalies, may then be found in the filtrate. [If an insoluble silicate containing alkali metals is mixed in the state of powder with 8 times its weight of precipitated *calcium carbonate* and its own weight of *ammonium chloride*, and the mixture is heated to redness in a covered platinum crucible for half an hour, too high a heat being avoided, a somewhat sintered mass is obtained, which, on being digested in hot water, falls to powder, and yields a solution containing, besides calcium chloride and hydroxide, all the alkalies of the silicate in the form of chlorides (J. Lawrence Smith).]

5. If *hydrofluoric acid*, in concentrated aqueous solution or in the gaseous state, is made to act upon silicic oxide, silicon fluoride gas escapes: $SiO_2 + 4HF = SiF_4 + 2H_2O$. The dilute acid dissolves silica to hydrofluosilicic acid: $SiO_2 + 6HF =$

$H_2SiF_6 + 2H_2O$. If this solution is evaporated to dryness, and if the silicic and hydrofluoric acids were pure, and the latter was in excess, no residue is left. Hydrofluoric acid acting upon silicates gives rise to the formation of silicofluorides: $CaSiO_3 + 6HF = CaSiF_6 + 3H_2O$. By heating with sulphuric acid, these are changed to sulphates, with evolution of hydrofluoric acid and silicon fluoride gases. If the powdered silicate is mixed with 3 parts of ammonium fluoride, or 5 parts of calcium fluoride in powder, the mixture made into paste with concentrated sulphuric acid, and heat is applied until no more fumes escape, the whole of the silicic acid present volatilizes as silicon fluoride. The bases are found in the residue as sulphates, mixed, if calcium fluoride was used, with calcium sulphate. All the experiments described in 5 should be performed in *platinum vessels*, and the evaporations must be made under a good *hood*, or better still in the *open air*.

6. On mixing 1 part of finely powdered silica, or a silicate, with 2 parts of powdered cryolite or fluor-spar (free from silica), and 4 or 5 parts of concentrated sulphuric acid, heating the mixture moderately in a platinum crucible, but not allowing it to spurt, and then holding close over the surface the loop of a stout platinum wire which has been freshly ignited, and now contains a drop of water, a pellicle of silicic acid will soon form on the latter from decomposition of the escaping silicon fluoride (BARFOED).

7. If silicic oxide or a silicate is fused with a small proportion of *sodium carbonate* in the loop of a platinum wire, FROTHING is observed in the bead, owing to the evolution of carbon dioxide. The bead obtained with pure silicic acid, or silicic anhydride, is always clear when hot; and with silicates rich in silicic acid (as the feldspathic rocks), the bead is also clear; otherwise it is opaque. The clearness of the cold bead depends upon the proportion between silicic acid, soda, and other bases.

8. *Sodium metaphosphate* in a state of fusion nearly fails to dissolve silicic oxide. If, therefore, silicic acid or a silicate (best in small fragments) is fused with sodium metaphosphate on a platinum wire, the bases are dissolved, while generally the greater part of the silicic oxide separates and floats about in a clear bead as a more or less translucent mass, exhibit-

ing the shape of the fragment of substance used, and forming the so-called SILICA SKELETON.

9. In regard to the microchemical detection of silicic acid, see HAUSHOFER, p. 120; BEHRENS, Zeitschr. f. analyt. Chem., **30**, 157.

§ 181.

Recapitulation and Remarks.—Carbon dioxide or free *carbonic acid* is readily known by the reaction with lime- or baryta-water; while the carbonates are easily detected by the evolution of a scarcely odorous gas when they are treated with acids. Many carbonates (*e.g.*, magnesite) are decomposed by acids only upon heating. When operating upon compounds which evolve other gases besides carbon dioxide, the gas should be tested with lime-water or baryta-water. *Silicic acid*, both in the free state and in silicates, may usually be readily detected by the reaction with sodium metaphosphate. In the form in which it is always obtained in analyses, it differs from all other bodies by its insolubility in acids (except hydrofluoric acid) and in fusing potassium disulphate, and its solubility in boiling solutions of alkalies and alkali carbonates; and from many bodies (especially from alumina and titanic oxide), by completely volatilizing upon repeated evaporation in a platinum dish, with hydrofluoric acid (or ammonium fluoride) and sulphuric acid.

Second Group of Inorganic Acids.

ACIDS WHICH ARE PRECIPITATED BY SILVER NITRATE, BUT NOT BY BARIUM CHLORIDE: *Hydrochloric Acid*, *Hydrobromic Acid*, *Hydriodic Acid*, *Hydrocyanic Acid*, *Hydroferro-* and *Hydroferricyanic Acid*, *Hydrosulphocyanic Acid*, *Hydrosulphuric Acid* (Nitrous Acid, Hypochlorous Acid, Chlorous Acid, Hypophosphorous Acid).

The silver compounds, corresponding to the *halogen* and *sulphur acids* of this group, are insoluble in dilute nitric acid. These acids react with metallic oxides and hydroxides, the metals combining with the chlorine, bromine, iodine, cyanogen, or sulphur, etc., while the oxygen of the metallic oxide, or the

hydroxyl of the hydroxide, forms water with the hydrogen of the acid.

§ 182.

a. Hydrochloric Acid, HCl.

1. Chlorine is a heavy, yellowish-green gas of a disagreeable and suffocating odor, which has a most injurious action upon the respiratory organs. It destroys many vegetable colors (litmus, indigo-blue, etc.), is not inflammable, and supports the combustion of a few bodies only. Minutely divided antimony, tin, etc., spontaneously ignite in it, and are converted into chlorides. It dissolves rather freely in water; and the chlorine-water formed has a faint yellowish-green color, smells strongly of the gas, bleaches vegetable colors, is decomposed by the action of light (§ 30), and loses its odor when shaken with mercury, the latter being partly converted into mercurous chloride. Small quantities of free chlorine may be readily detected in a liquid by adding it to a dilute solution of indigo having only a faint blue color, which is decolorized by the action of the free chlorine, or also, in the absence of nitrous acid, by the blue color imparted to a mixture of starch paste and potassium iodide (see § 184, 9).

2. Hydrochloric acid, at the common temperature and common atmospheric pressure, is a colorless gas, which forms dense fumes in moist air, is suffocating and very irritating, and dissolves in water with exceeding facility. The concentrated aqueous solution (fuming hydrochloric acid) loses a large portion of its gas upon heating.

3. The normal metallic chlorides are readily soluble in water, with the exception of lead, silver, cuprous, and mercurous chlorides, and most of them are white or colorless. Many chlorides volatilize at a high temperature, without suffering decomposition; while others are decomposed upon ignition, and some are fixed at a moderate red heat.

4. Even in highly dilute solutions of free hydrochloric acid or of almost all metallic chlorides, *silver nitrate* produces a white precipitate of silver chloride, AgCl, which upon exposure to light becomes first violet, then black. It is insoluble in dilute

nitric acid, but dissolves readily in ammonia as well as in potassium cyanide solution, and also in a boiling solution of ammonium "sesqui"-carbonate* (H. HAGER). [Placed in contact with metallic zinc and water slightly acidulated with sulphuric acid, silver chloride is decomposed, soluble zinc chloride and metallic silver being formed.] Silver chloride fuses without decomposition (compare § 135, 7). From a solution of green chromium chloride, chlorine is incompletely precipitated by means of silver nitrate (PÉLIGOT), and it is not precipitated from a solution of molybdenous oxychloride in sulphuric acid (BLOMSTRAND). From a solution of auric chloride, even in the presence of nitric acid, silver nitrate produces an ochre-yellow precipitate, containing gold, silver, and chlorine.

5. In solutions containing free hydrochloric acid or metallic chlorides, *mercurous nitrate* and *lead acetate* produce precipitates of MERCUROUS CHLORIDE, Hg_2Cl_2, and LEAD CHLORIDE, $PbCl_2$. For the properties of these precipitates, see § 136, 6, and § 137, 7. Lead acetate precipitates lead auric chloride from a solution of hydrochlorauric acid.

6. If hydrochloric acid is heated with *manganese dioxide* or *lead dioxide*, or a chloride with *manganese dioxide* or *lead dioxide* and rather concentrated *sulphuric acid*, CHLORINE is evolved, which may be readily recognized by its odor, its yellowish-green color, and its bleaching action upon vegetable colors. The best way of testing the latter is to expose to the gas a moist strip of litmus-paper, or of paper colored with solution of indigo. When chlorides are heated with manganese or lead dioxide and acetic acid, no chlorine is evolved.

7. If a metallic chloride is triturated with half its weight or somewhat more of *potassium dichromate*, the dry mixture treated with *concentrated sulphuric acid* in a tubulated retort, and a gentle heat applied, the deep brownish-red gas of CHROMIC OXYCHLORIDE, CrO_2Cl_2 (CHLOROCHROMIC ACID), is evolved, which condenses into a fluid of the same color, and passes into the receiver. If this distillate is mixed with ammonia in excess, a yellow-colored liquid is produced from the formation of ammo-

* To prepare this, dissolve 1 part of the transparent ammonium carbonate of commerce in 9 parts of water of ordinary temperature, and add, for each 10 cc of the liquid, 5 drops of ammonia-water of .96 sp. gr.

nium chromate: $CrO_2Cl_2 + 4NH_4OH = 2NH_4Cl + (NH_4)_2CrO_4 + 2H_2O$. Upon addition of an acid, the color of the solution changes to a reddish-yellow, owing to the formation of acid ammonium chromate.

8. Chlorine is detected in the metallic chlorides insoluble in water and nitric acid by fusing them with *sodium-potassium carbonate*, and treating the mass with water, which dissolves the sodium and potassium chlorides formed in the process, together with the excess of the sodium and potassium carbonates.

9. If *cupric oxide* is dissolved in a bead of *sodium metaphosphate* on a platinum wire in the outer blowpipe flame, in sufficient quantity to make the mass nearly opaque, a trace of a substance containing chlorine added to it while still in fusion, and the bead then exposed to the reducing flame, a fine BLUE-COLORED flame, inclining to PURPLE, will be seen encircling it as long as chlorine is present (BERZELIUS).

10. In relation to the microscopic detection of chlorine, see HAUSHOFER, p. 47; BEHRENS, Zeitschr. f. analyt. Chem., **30**, 170; A. PERCY SMITH, Pharmac. Centralhalle, 1886, p. 638.

§ 183.

b. HYDROBROMIC ACID, HBr.

1. BROMINE is a heavy, brownish-red liquid of a very disagreeable, chlorine-like odor; it boils at 63°, and volatilizes rapidly even at the common temperature. The vapor is brownish-red. Bromine bleaches vegetable colors like chlorine, is rather soluble in water, dissolves still more readily in alcohol, and very freely in ether, carbon disulphide, and chloroform. The solutions are yellowish-red. Ether, carbon disulphide, or chloroform, when shaken with an aqueous solution of bromine, extract the latter from it.

2. HYDROBROMIC ACID GAS, its AQUEOUS SOLUTION, and the METALLIC BROMIDES, in their general deportment, show a great analogy to the corresponding chlorides.

3. In aqueous solutions of hydrobromic acid or of bromides, *silver nitrate* produces a yellowish-white precipitate of SILVER BROMIDE, AgBr, which becomes gray upon exposure to

light. This precipitate is insoluble in dilute nitric acid, and almost insoluble in a boiling solution of ammonium "sesqui"-carbonate (H. HAGER). Ammonia-water dissolves silver bromide, but much more difficultly than silver chloride. It dissolves with facility in potassium cyanide. [With metallic zinc and water acidulated with sulphuric acid, it yields soluble zinc bromide and metallic silver.]

4. In neutral solutions of metallic bromides, *palladious nitrate*, but not palladious chloride, produces a reddish-brown precipitate of PALLADIOUS BROMIDE, $PdBr_2$. In concentrated solutions, this precipitate is formed immediately; but in dilute solutions, it makes its appearance only after standing some time.

5. *Nitric acid* decomposes hydrobromic acid and the bromides, with the exception of silver bromide, upon the application of heat, and liberates the bromine by oxidizing the hydrogen or the metal. In the case of a solution, the liberated bromine colors it yellow or yellowish-red. With bromides in the solid state or in concentrated solution, brownish-red (if diluted, brownish-yellow) vapors of bromine escape at the same time, which, if evolved in sufficient quantity, condense in the cold part of the test-tube to small drops. In the cold, nitric acid, even when red and fuming, fails to liberate the bromine in very dilute solutions of bromides, nor is it liberated by solution of nitrous acid in concentrated sulphuric acid, nor by hydrochloric acid and potassium nitrite.

6. *Chlorine*, in the *gaseous* state or in *aqueous solution*, immediately liberates bromine in solutions of its compounds, the fluid assuming a yellowish-red tint if the quantity of bromine present is not too minute. A large excess of chlorine must be avoided, since this causes the formation of bromine chloride, which destroys the color wholly or nearly so. This reaction is made much more delicate by the addition of a fluid which dissolves bromine and does not mix with water, such as *carbon disulphide* or *chloroform*. Mix the neutral or feebly acid solution in a test-tube with a little of one of these fluids, sufficient to form a large drop at the bottom, then add dilute chlorine-water drop by drop, and shake the tube. With appreciable quantities of bromine (*e.g.*, 1 part in 1000 parts of water), the drop at the bottom acquires a reddish-yellow tint; but with very

minute quantities (1 part of bromine in 30,000 parts of water), a pale yellow tint, which, however, is still distinctly discernible.* Ether, which was previously used for the purpose, is *far less* well adapted for this reaction. A large excess of chlorine-water must be avoided in this experiment also, and it must always be ascertained first whether the chlorine-water, mixed with a large quantity of water and some carbon disulphide or chloroform, and shaken, will leave these solvents quite uncolored. If not, the reagent is not suited for the purpose. If the solution of bromine in carbon disulphide or chloroform (or ether) is mixed with some solution of potassium hydroxide, the mixture shaken, and heat applied, the yellow color disappears, and the solution now contains potassium bromide and bromate. By evaporation and ignition, the potassium bromate is converted into potassium bromide, and the ignited mass may then be further tested as directed in 7.

7. If bromides are heated with *manganese* or *lead dioxide* and concentrated or dilute *sulphuric acid*, BROWNISH-RED VAPORS OF BROMINE are evolved. In the presence of chlorides, it is necessary to operate with dilute solutions so that no bromine chloride can be formed. When heated with manganese dioxide and acetic acid, bromides give off no bromine, but they do evolve bromine when heated with lead dioxide and acetic acid (VORTMANN). If the bromine is present only in very minute quantity, the color of the escaping vapor is not visible; but if the mixture is heated in a small retort, and the vapors are transmitted through a long glass condenser, the color of the bromine may generally be seen by looking lengthwise through the tube. The first drops of the distillate are also colored yellow, and these together with the first vapors should be received in a test-tube containing some starch moistened with water; since,

8. If moistened *starch* is brought into contact with free bromine, more especially in the form of vapor, YELLOW BROMIZED STARCH is formed. The coloration is not always instantaneous. The reaction is rendered most delicate by sealing the test-tube

* In solutions of hydrobromides of the alkaloids, the reaction does not take place. The alkaloids are therefore to be first removed by means of sodium hydroxide or carbonate solution, etc. (A. WELLER, Zeitschr. f. analyt. Chem., 26, 740).

which contains the moistened starch and the first drops of the distillate from 7, and then cautiously inverting it, so as to cause the moist starch to occupy the upper part of the tube, while the fluid is at the bottom. The presence of even the slightest trace of bromine will now, in the course of from twelve to twenty-four hours, impart a yellow tint to the starch, which, however, after some time will again disappear. The reaction may be called forth in a simpler manner, with almost the same degree of delicacy, by gently heating the fluid containing free bromine, or also the original mixture of bromide, manganese dioxide, and sulphuric acid, in a very small beaker covered with a watch-glass having a strip of paper attached to the lower side, moistened with starch paste and sprinkled with starch powder.

9. If concentrated *sulphuric acid* is poured over a mixture of a bromide with *potassium dichromate*, and heat is then applied, a brownish-red gas is evolved, exactly as in the case of chlorides. But this gas consists of pure BROMINE, and therefore the fluid passing over does not turn yellow, but becomes colorless upon supersaturation with ammonia. Bromine may also be expelled from solutions by heating with potassium chromate and sulphuric acid.

10. If a solution of hydrobromic acid or an alkali-metal bromide is mixed with a little *gold chloride* solution, a straw or dark orange color is produced from the formation of GOLD BROMIDE. If iodine is present, it must be removed before the solution of gold is added (BILL).

11. In order to detect bromine in them, the metallic bromides which are insoluble in water and nitric acid are treated in the same way as the corresponding chlorides.

12. If a substance containing bromine is added to a *sodium metaphosphate bead saturated with cupric oxide*, and the bead is then ignited in the inner blowpipe flame, the flame is colored BLUE, inclining to GREEN, more particularly at the edges (BERZELIUS).

13. In relation to the microscopic detection of bromine, see BEHRENS, Zeitschr. f. analyt. Chem., **30**, 170; A. PERCY SMITH, Pharmac. Centralhalle, 1886, p. 638.

§ 184.

c. Hydriodic Acid, HI.

1. Iodine is a soft solid body, with a peculiar, disagreeable odor. It generally occurs in the form of black, shining, crystalline scales. It fuses at 114°, boils above 200°, giving iodine vapor, which has a beautiful violet-blue color, and condenses upon cooling to a black sublimate. It is very sparingly soluble in water, but readily in alcohol, ether, carbon disulphide, and chloroform, as well as in aqueous solution of potassium iodide. The aqueous solution is light brown, the alcoholic, ethereal, and potassium iodide solutions are deep red-brown, while those in carbon disulphide and chloroform are violet-red. Iodine destroys vegetable colors, only slowly and imperfectly. It stains the skin brown, and with starch forms a compound of a most intense, dark blue color. This always results when iodine vapor or a solution containing free iodine is brought into contact with starch, best in the form of starch paste. The color of iodized starch is destroyed by alkalies, by chlorine and bromine, and by sulphurous acid and other reducing agents.

2. Hydriodic acid gas resembles hydrochloric and hydrobromic acid gases, and dissolves copiously in water. The colorless solution of hydriodic acid turns speedily to a reddish-brown in contact with the air, water and a solution of iodine in hydriodic acid being formed.

3. The iodides also correspond in many respects with the chlorides. Of the iodides of the heavy metals, however, many more are insoluble in water than is the case with the corresponding chlorides. Many iodides have characteristic colors, *e.g.*, lead iodide, mercurous iodide, and mercuric iodide.

4. In aqueous solutions of hydriodic acid and of iodides, *silver nitrate* produces yellowish-white precipitates of silver iodide, AgI, which blacken on exposure to light. Silver iodide is insoluble in dilute nitric acid, scarcely soluble in ammonia-water containing 5 per cent of ammonia, and not soluble in a boiling solution of ammonium "sesqui"-carbonate (H. Hager). It dissolves readily in potassium cyanide [and with zinc and dilute sulphuric acid, reacts like silver chloride and bromide].

5. Even in very dilute solutions of hydriodic acid or metallic iodides, *palladious chloride* and *palladious nitrate* produce a brownish-black precipitate of PALLADIOUS IODIDE, PdI_2, which dissolves to a trifling extent in saline solutions (sodium chloride, magnesium chloride, etc.), but is insoluble or nearly so in dilute, cold hydrochloric and nitric acids.

6. From neutral aqueous solutions of the iodides, a solution of 1 part of *cupric sulphate* and $2\frac{1}{2}$ parts of *ferrous sulphate* throws down CUPROUS IODIDE, Cu_2I_2, in the form of a dirty white precipitate. The addition of ammonia promotes the complete precipitation of the iodine. Chlorides and bromides are not precipitated by this reagent. Instead of using the above mixture of sulphates, cupric sulphate alone may be added, and afterwards enough sulphurous acid or acid sodium sulphite to remove the brown color produced by separated iodine.

7. Pure *nitric acid*, free from nitrous acid, decomposes hydriodic acid or iodides, only when acting upon them in its concentrated form, particularly when aided by the application of heat. But *nitrous acid* and *nitrogen peroxide* decompose hydriodic acid and iodides with the greatest facility, even in the most dilute solutions. Colorless solutions of iodides therefore acquire immediately a brownish-red color upon addition of some red fuming nitric acid, or of a mixture of this with concentrated sulphuric acid, or better still, upon addition of a solution of nitrous acid in concentrated sulphuric acid, or of potassium nitrite and some sulphuric or hydrochloric acid. From more concentrated solutions, the iodine separates in the form of black scales, while nitrogen oxides and iodine vapor escape.*

8. As the blue coloration of iodized starch remains visible in much more highly dilute solutions than the yellow color of solution of iodine in water, the delicacy of the reaction just described (7) is considerably heightened by first mixing the fluid to be tested for iodine with some thin, tolerably clear *starch paste*, then adding a few drops of dilute sulphuric acid, to make the fluid strongly acid, and finally one of the reagents given in 7. Of the solution of nitrous acid in concentrated sulphuric

* From cyanogen iodide, iodine is not separated by oxidizing agents, but it is set free by reducing agents (E. v. MEYER, Zeitschr. f. analyt. Chem., **27**, 229).

acid, a single drop on a glass rod suffices to produce the reaction most distinctly, and I can, therefore, recommend this reagent most highly, as does Fr. J. Otto, who first proposed its use. Red fuming nitric acid must be added in somewhat larger quantity to call forth the reaction in its highest intensity; therefore, this reagent is not well adapted to detect very minute quantities of iodine. The reaction with potassium nitrite also is very delicate. The fluid to be tested is mixed with dilute sulphuric acid or with hydrochloric acid to distinctly acid reaction, and a drop or two of a concentrated solution of potassium nitrite is then added in the presence of a little starch paste. In cases where the quantity of iodine present is very minute, the fluid turns reddish, instead of blue. An excess of the fluid containing nitrous acid does not materially impair the delicacy of the reaction. As iodized starch becomes colorless in hot water, the fluids must of necessity be cold, and the colder they are the more delicate the reaction. To attain the highest degree of delicacy, cool the fluid with ice, let the starch deposit, and place the test-tube upon white paper to observe the reaction (compare also "Recapitulation and Remarks" below, § 188).

9. *Chlorine gas* and *chlorine-water* decompose compounds of iodine also, setting the iodine free; but if the chlorine is applied in excess, the liberated iodine combines with it to iodine chloride. A dilute solution of a metallic iodide, mixed with starch paste, acquires at once, therefore, upon addition of a little chlorine-water, a blue tint, but becomes colorless again upon addition of more chlorine-water. As it is difficult not to exceed the proper limit, especially where the quantity of iodine present is only small, chlorine-water is not well adapted for the detection of minute quantities of iodine.

10. If a solution containing hydriodic acid or an iodide, acidified if necessary, is mixed with *chloroform* or *carbon disulphide*, so as to leave a large drop undissolved, and one of the agents by which iodine is liberated (a drop of a solution of nitrous acid in sulphuric acid, hydrochloric acid and potassium nitrite, chlorine-water, etc.) is added, the mixture vigorously shaken, and then allowed to stand at rest, the chloroform or the carbon disulphide, colored violet-red by the iodine dissolved in it, subsides to the bottom. This reaction, also, is exceedingly

delicate. If a solution containing free iodine is shaken with *petroleum oil*, *benzol*, or *ether*, the first two are colored almost red, and the ether more reddish-brown or yellow. (Iodine colors ether much more intensely than an equal amount of bromine.)

11. If metallic iodides are heated with *concentrated sulphuric acid*, or with *manganese* or *lead dioxide* and *dilute sulphuric acid* or even *acetic acid*, or with *dilute sulphuric acid* and *potassium dichromate*, or with *ferric chloride* or *ferric sulphate*, iodine separates, and may be recognized by the color of its vapor, or in the case of very minute quantities, by its action upon a strip of paper coated with starch paste.

12. Upon fusion with *sodium carbonate*, the iodides which are insoluble in water and nitric acid comport themselves in the same manner as the corresponding chlorides.

13. A *sodium metaphosphate bead, saturated with cupric oxide*, when charged with a substance containing iodine, and ignited in the inner blowpipe flame, imparts an intense GREEN color to the flame.

14. In regard to the microscopic detection of iodine, see HAUSHOFER, p. 52; BEHRENS, Zeitschr. f. analyt. Chem., **30**, 171; DENIGÈS, Chem. Centralbl., 1894, I, p. 104.

§ 185.

d. HYDROCYANIC ACID, HCN.

1. CYANOGEN, C_2N_2, is a colorless gas of a peculiar, penetrating odor. It burns with a crimson flame, is rather soluble in water, and has a specific gravity of 1.8.

2. HYDROCYANIC ACID (prussic acid) is a colorless, volatile, inflammable liquid, the stupefying odor of which distantly resembles that of bitter almonds. It is miscible with water in all proportions, and in the pure state, it speedily suffers decomposition. It is extremely poisonous, and the aqueous solution does not redden litmus-paper.

3. The CYANIDES of the alkali and alkali-earth metals are soluble in water, and the solutions smell of hydrocyanic acid. They are readily decomposed by acids, even by carbonic acid. At 50° to 80°, mercuric cyanide, and at 100°, finely divided cyanides,

suspended in water and insoluble in it, are decomposed by carbonic acid (H. Hilger and K. Tamba). When ignited with exclusion of air, potassium and sodium cyanides fuse without decomposition; but when fused with oxides of lead, copper, antimony, tin, and many other oxides, they reduce these, and are converted into cyanates. Upon fusion with almost every metallic sulphide, a metallic sulphocyanide is produced. Only a few of the cyanides of heavy metals are soluble in water; but all of them are decomposed by ignition, the cyanides of the noble metals being converted into cyanogen gas and metal or metallic paracyanide, and the cyanides of the other heavy metals, into nitrogen gas and metallic carbides. Many of the cyanides of heavy metals are not decomposed by dilute oxygen acids, and only with difficulty by concentrated nitric acid. By heating and evaporation with concentrated sulphuric acid, all cyanides are decomposed; while hydrochloric acid decomposes a few, and hydrogen sulphide decomposes many.

4. The cyanides have a great tendency to combine with each other; hence most of the cyanides of the heavy metals dissolve in potassium cyanide. The resulting compounds are either:

a. Double salts, *e.g.*, potassium nickel cyanide, $2KCN.Ni(CN)_2$. From solutions of such double salts, acids precipitate the metallic cyanide, by decomposing the potassium cyanide which was combined with it. Or,

b. Compounds which behave like simple halogen salts, in which a metal (*e.g.*, potassium) is combined with a compound radical consisting of cyanogen and another (metal iron, cobalt, manganese, chromium). The ferro- and the ferricyanides of potassium, $K_4Fe(CN)_6$ and $K_3Fe(CN)_6$, are compounds of this kind. From solutions of such compounds, dilute acids do not separate metallic cyanides in the cold. If the potassium is replaced by hydrogen, corresponding hydrogen acids are formed, which must not be confounded with hydrocyanic acid.

The reactions of hydrocyanic acid and the simple cyanides will first be considered; then, in an appendix to this paragraph, those of hydroferro- and hydroferricyanic acid and also of hydrosulphocyanic acid.

5. *Silver nitrate* produces in solutions of free hydrocyanic acid and of cyanides of the alkali metals, white precipitates of

SILVER CYANIDE, AgCN, which are readily soluble in potassium cyanide, dissolve with some difficulty in ammonia, and are insoluble in dilute nitric acid. These precipitates are decomposed by ignition, leaving metallic silver with some silver paracyanide. When free hydrocyanic acid is present, the delicacy of this reaction is increased by first adding ammonia in excess, then silver nitrate, and finally acidifying with nitric acid.

6. If a solution of *ferrous sulphate* and a drop of *ferric chloride* solution are added to a solution of free hydrocyanic acid, no alteration takes place; but if a few drops of a *solution of potassium* or *sodium hydroxide* are now added, until the liquid just reacts alkaline, a bluish-green precipitate forms, which consists of a mixture of Prussian blue (compare § 127, 6) and ferrous-ferric hydroxide. Upon now acidifying with hydrochloric acid, the ferrous-ferric hydroxide dissolves, while the PRUSSIAN BLUE remains undissolved. If only a very minute quantity of hydrocyanic acid is present, the fluid simply appears green after the addition of the hydrochloric acid, and it is only after long standing that a trifling blue precipitate separates from it. The same final reaction is observed when a mixture of ferrous and ferric salt is mixed with the solution of an alkali-metal cyanide, and hydrochloric acid is then added.

7. If a liquid containing a little hydrocyanic acid or alkali-metal cyanide is mixed with sufficient yellow ammonium sulphide to impart a yellowish tint to the fluid, after the addition of a drop of weak potassium or sodium hydroxide solution when free hydrocyanic acid was present, and the mixture is warmed in a porcelain dish upon the water-bath until it has become colorless and the excess of ammonium sulphide is decomposed or volatilized, and finally evaporated to dryness, the residue now contains ammonium sulphocyanide. This is dissolved in a little water, made acid with 2 or 3 drops of hydrochloric acid, allowed to stand a few minutes, and then a little ferric chloride is added. A blood-red coloration shows the presence of the sulphocyanogen which has been formed. Should a violet color appear, or should the resulting red color disappear quickly, some more ferric chloride must be added to call forth the reaction (LIEBIG, ALMÉN). This reaction is exceedingly delicate. The following equation expresses the transformation

of a cyanide into a sulphocyanide: $(NH_4)_2S_2 + 4KCN = 4KCNS + (NH_4)_2S$. If an acetate is present, the reaction takes place only upon addition of more hydrochloric acid. To discover the cyanogen in *insoluble compounds* by converting it into ferric sulphocyanide, proceed as follows: Fuse some sodium thiosulphate in the loop of a platinum wire in an alcohol flame, until the water of crystallization has escaped and the mass swells up, introduce a small portion of the substance, heat for a little time, removing it from the flame as soon as the sulphur begins to burn, and then dip the mass into a few drops of ferric chloride mixed with water and a little hydrochloric acid. A permanent, blood-red color will be produced if cyanogen was present. If the substance is heated too long, the reaction fails, as the sodium sulphocyanide formed is then destroyed. This method is well suited to distinguish silver chloride, bromide, or iodide from cyanide (A. Fröhde).

8. If, to a liquid containing hydrocyanic acid or a metallic cyanide, a few drops of a solution of *potassium nitrite* are added, then from 2 to 4 drops of *ferric chloride* solution, and enough dilute sulphuric acid so that the brown color of the ferric salt formed at first just changes into light yellow, the liquid is then heated to incipient boiling, cooled, some ammonia added to precipitate the iron which is in excess, the precipitate filtered off, and one or two drops of hydrogen sulphide water are added to the filtrate (which should still contain free ammonia), the solution takes on a violet color from the action of the sulphide upon the potassium nitroprusside which has been formed (G. Vortmann).

9. On mixing a moderately concentrated solution of an alkali-metal cyanide with a little *picric acid* solution (1 part of picric acid to 250 parts of water) and boiling, the fluid appears dark red from formation of alkali-metal picrocyaminate (isopurpurate), the coloration increasing in intensity by standing. If the solution of the cyanide is very dilute, no more picric acid must be added than is just sufficient to color the fluid yellow. After boiling, the red coloration often does not make its appearance till the fluid has cooled and stood for some time (C. D. Braun). The reaction is not as delicate as those described in 6, 7, and 8, but it may be used for the detection of an alkali-metal

cyanide in the presence of potassium ferrocyanide, which does not give potassium picrocyaminate when treated in the same way.

10. On soaking filter-paper with *freshly prepared alcoholic tincture of guaiacum* containing 3 or 4 per cent of the resin, allowing the alcohol to evaporate, moistening the paper with solution of *copper sulphate* containing $\frac{1}{4}$ per cent of the salt, and then exposing it to air in which a trace of hydrocyanic acid is present, it becomes blue from liberation of active oxygen: $3CuO + 4HCN = Cu_2(CN)_2.Cu(CN)_2 + 2H_2O + O$ (PAGENSTECHER, SCHONBEIN). The reaction is exceedingly delicate, but it is not conclusive for hydrocyanic acid without confirmation, because the guaiacum-copper paper is also made blue by air containing ammonia, nitrous acid, ozone, bromine, iodine, and hypochlorous acid. It is still less conclusive when it is produced in solutions, for a mixture of guaiacum tincture with very dilute copper sulphate solution is turned blue, not only by hydrocyanic acid and cyanides, but also by soluble lower chlorides, bromides, iodides, fluorides, etc.

11. If a very dilute solution of *iodized starch* is mixed with a trace of hydrocyanic acid, or, after addition of dilute sulphuric acid, with a trace of an alkali-metal cyanide, the blue color disappears immediately or after a short time, the iodine and the hydrocyanic acid being transformed into cyanogen iodide and hydriodic acid (SCHÖNBEIN). This is a very delicate reaction, but cannot be relied upon without further tests, as many other substances decolorize iodized starch.

12. None of the above methods will serve to effect the detection of cyanogen in mercuric cyanide. To detect cyanogen in that compound, its solution is mixed with hydrogen sulphide, when mercuric sulphide precipitates, and the solution contains free hydrocyanic acid. In solid mercuric cyanide, the cyanogen is most readily detected by heating in a glass tube (compare 3). Upon heating a solution of mercuric cyanide with hydrochloric acid, with sodium chloride and oxalic acid, or with sodium chloride and dilute sulphuric acid, in a distilling apparatus, a large part of the cyanogen is obtained in the distillate as hydrogen cyanide. In the presence of small amounts, it is best to distil with tartaric acid and a little hydrogen sulphide (AUTHENRIETH).

13. Regarding the microscopic detection of hydrogen cyanide, see BEHRENS, Zeitschr. f. analyt. Chem., **30**, 166.*

Appendix to Hydrocyanic Acid.

§ 186.

a. Hydroferrocyanic acid, $H_4Fe(CN)_6$. Hydroferrocyanic acid is colorless, crystalline, and readily soluble in water. Its solution has a strong acid reaction. Some of the ferryocyanides, as those containing alkali and alkali-earth metals, are soluble in water, but the greater number of them are insoluble in that liquid. All ferrocyanides are decomposed by ignition; and where they are not quite anhydrous, hydrocyanic acid, carbonic acid, and ammonia escape; otherwise, nitrogen and occasionally cyanogen. In aqueous solutions of hydroferrocyanic acid or ferrocyanides, *ferric chloride* produces a blue precipitate of FERRIC FERROCYANIDE (Prussian blue, compare § 127, 6); and *cupric sulphate*, a brownish-red precipitate of CUPRIC FERROCYANIDE (compare § 140, 9). *Silver nitrate* gives a white precipitate of SILVER FERROCYANIDE, $Ag_4Fe(CN)_6$, which is insoluble in nitric acid and in ammonia (upon short action in the cold), but dissolves in potassium cyanide. Upon boiling with aqueous ammonia, silver ferrocyanide yields ferrous oxide, while the solution contains silver cyanide and ammonium cyanide (WEITH). If a not too dilute solution of an alkali-metal ferrocyanide is mixed with *hydrochloric acid*, and some *ether* is poured on the top of the mixture HYDROFERROCYANIC ACID separates in the crystalline form where the two fluids meet. Alkali-metal ferrocyanides are not decomposed by *carbonic acid* in aqueous solution in the cold (difference from the cyanides), but they are decomposed at from 72° to 74° (AUTHENRIETH). Prussian blue and cupric ferrocyanide suspended in water, however, do not decompose with carbonic acid below 100°. Upon *boiling with water*, soluble ferrocyanides, as well as those which are insoluble but finely divided, are de-

* Concerning the detection of cyanogen in flames, compare C. LUDEKING, Zeitschr. f. analyt. Chem., 29, 342.

composed, even without the aid of carbonic acid, with the formation of hydrogen cyanide (A. HILGER and K. TAMBA). Solutions of metallic ferrocyanides which are made alkaline with sodium carbonate give no prussic acid when distilled in a stream of *carbonic acid*, nor is any hydrogen cyanide obtained by the distillation of a ferrocyanide with *hydrogen sodium carbonate* (JACQUEMIN). Upon warming, ferrocyanides in acidified solutions are converted by hydrogen peroxide into ferricyanogen compounds (WELTZIEN). Insoluble ferrocyanides are decomposed by boiling with solution of *sodium hydroxide*, sodium ferrocyanide being formed, and the metals separating as hydroxides, unless they are soluble in sodium hydroxide. Upon heating *ammoniacal silver solution* with ferrocyanogen compounds (*e.g.*, Prussian blue), ferric oxide separates. The solution then gives a precipitate of silver cyanide upon acidifying it with nitric acid (WEITH). If ferrocyanides are heated with a mixture of 3 parts concentrated sulphuric acid and 1 part water till the free acid is expelled, they are decomposed, and the cyanogen is driven off in the form of hydrocyanic acid, while the metals remain behind as sulphates. On projecting metallic ferrocyanides into fusing potassium nitrate, the cyanogen is converted into carbon dioxide and nitrogen, and the metals are converted into oxides, which remain in the crucible.

b. Hydroferricyanic acid, $H_6Fe_2(CN)_{12}$. Hydroferricyanic acid and many of the ferricyanides are soluble in water; and all ferricyanides are decomposed by ignition similarly to the ferrocyanides. In the aqueous solutions of hydroferricyanic acid and its salts, *ferric chloride* produces no blue precipitate (§ 127, 7), but *ferrous sulphate* produces a blue precipitate of FERROUS FERRICYANIDE (compare § 126, 8). Cupric *sulphate* gives a yellowish-green precipitate of CUPRIC FERRICYANIDE, $Cu_3Fe_2(CN)_{12}$, which is insoluble in hydrochloric acid; and *silver nitrate* yields an orange-colored precipitate of SILVER FERRICYANIDE, $Ag_6Fe_2(CN)_{12}$, which is insoluble in nitric acid, but dissolves readily in ammonia and in potassium cyanide. The aqueous solutions of alkali-metal ferricyanides behave like the corresponding ferrocyanogen compounds, when they are boiled with water, or when *carbonic acid* or *hydrogen sodium carbonate* acts upon them. *Hydrogen sulphide* decomposes the alkali-metal

ferricyanides, with separation of sulphur and the formation of alkali-metal ferrocyanides and hydroferrocyanic acid. Free hydroferricyanic acid suffers a similar decomposition, and consequently, also, a solution of potassium ferricyanide to which hydrochloric acid is added. Ferricyanides in alkaline solution are reduced by *hydrogen peroxide* to ferrocyanogen compounds, with evolution of oxygen (WELTZIEN). The insoluble ferricyanides are decomposed by boiling in solution of sodium hydroxide. In the fluid filtered off from the separated metallic oxides, either sodium ferricyanide alone is found, or a mixture of sodium ferro- with ferricyanide. The ferricyanogen compounds are decomposed by *ammoniacal silver solution* like the ferrocyanogen compounds, and nitric acid precipitates silver cyanide from the ammoniacal filtrate. By heating with a mixture of 3 parts concentrated *sulphuric acid* and 1 part water, and also by fusing with *potassium nitrate*, the ferricyanides are decomposed like the ferrocyanides.

c. Hydrosulphocyanic (or *thiocyanic*) *acid*, HCNS. This forms a colorless, oily liquid, which solidifies in crystals at — 12.5°, and, according to ARTUS, boils at 85°. It has a penetrating odor similar to acetic acid, and dissolves in water as well as in alcohol, forming liquids with an acid reaction. It acts as a poison, and gradually decomposes into hydrogen cyanide and yellow, crystalline perthiocyanic acid, $H_2C_2N_2S_3$. By the action of much concentrated hydrochloric acid upon a concentrated aqueous solution of hydrosulphocyanic acid (or also potassium sulphocyanide), this decomposition completes itself rapidly. Hydrosulphocyanic acid forms sulphocyanides (thiocyanates) with bases. Most of these are soluble in water, and their neutral aqueous solutions are not, or are scarcely, decomposed by boiling. Upon boiling with alkali-metal acid carbonates, ammonium carbonate is formed, but no hydrogen cyanide. By distilling with dilute sulphuric acid, phosphoric acid, or tartaric acid, a part of the sulphocyanogen is obtained in the distillate as dilute hydrosulphocyanic acid, but the rest is decomposed. Upon heating with dilute nitric acid, a violent decomposition takes place, accompanied by the liberation of nitric oxide and carbonic acid, and the formation of sulphuric acid. When ignited with access of air, all metallic sulphocyanides are decomposed, and yield, according to the

nature of the bases, sulphur dioxide, sulphates, and cyanates, or nitrogen, cyanogen, carbon disulphide, and metallic sulphides.

Solutions of hydrosulphocyanic acid or of metallic sulphocyanides are colored blood-red by *ferric chloride* solution acidified with hydrochloric acid (§ 127, 8). In concentrated solutions of alkali-metal sulphocyanides, *copper sulphate* produces a velvet-black precipitate of CUPRIC SULPHOCYANIDE, $Cu(CNS)_2$, while, if the solutions are dilute, only an emerald-green coloration is produced. *Copper sulphate* solution mixed with an excess of *sulphurous acid* throws down, even from very dilute solutions, pale, reddish-white CUPROUS SULPHOCYANIDE (§ 140, 10). *Silver nitrate* produces a white, curdy precipitate of SILVER SULPHOCYANIDE, AgCNS, insoluble in dilute nitric acid, but soluble in ammonia. *Mercurous nitrate* produces, according to the proportions and the concentration, a gray or white precipitate. The latter is MERCUROUS SULPHOCYANIDE, $Hg_2(CNS)_2$. With metallic *zinc*, hydrosulphocyanic acid or the acidified solution of a sulphocyanide gives HYDROGEN SULPHIDE.

§ 187.

e. Hydrosulphuric Acid (Hydrogen Sulphide), H_2S.

1. Sulphur is usually a solid, brittle, friable, tasteless body, insoluble in water. It occasionally occurs in the form of yellow or brownish crystals, or crystalline masses of the same colors, and sometimes as a yellow, yellowish-white, or grayish-white powder. It melts at 118°; and upon the application of a stronger heat, it is converted into a brownish-yellow vapor, which in cold air condenses to a yellow powder, and on the sides of the vessel to drops. Heated in the air, it burns with bluish flame to sulphur dioxide, which betrays its presence at once by its suffocating odor. Concentrated nitric acid, bromine in hydrochloric acid, nitro-hydrochloric acid, and a mixture of potassium chlorate and hydrochloric acid dissolve sulphur gradually, with the aid of a moderate heat, and convert it into sulphuric acid. In boiling solution of sodium hydroxide, sulphur dissolves to a yellow fluid, which contains sodium sulphide and sodium thiosulphate. It is insoluble in cold aqueous ammonia, but in warm

ammonia, it dissolves to a small extent. Carbon disulphide, benzol, and petroleum-ether dissolve the ordinary variety of sulphur with ease, but there is a kind which is insoluble in these solvents. A hydrogen flame when brought into contact with sulphur (but also with sulphides or sulphates) shows a fine blue inner flame.

2. HYDROSULPHURIC ACID, or HYDROGEN SULPHIDE, at the common temperature and under common atmospheric pressure, is a colorless, poisonous, inflammable gas, soluble in water, and readily recognized by its odor of rotten eggs. It transiently imparts a red tint to moist litmus-paper. When it is kindled, it burns with a blue flame to water and sulphur dioxide. *Hydrogen sulphide water*, the properties of which have been already given in § 33, is decomposed by chlorine, bromine, iodine, ferric chloride, permanganic acid, chromic acid, nitrous acid, and other oxidizing agents, with the separation of sulphur.

3. Of the SULPHIDES, only those of alkali and alkali-earth metals are soluble in water. These, as well as the sulphides of iron, manganese, and zinc, are decomposed by dilute mineral acids, with evolution of hydrogen sulphide gas, which may be readily detected by its smell, and by its action upon solution of lead (see 4). The decomposition of polysulphides is also attended with separation of sulphur in a finely divided state, and the white precipitate may be readily distinguished from other precipitates by its solubility in benzol or petroleum-ether. Part of the sulphides of the metals of the fifth and sixth groups are decomposed by concentrated and boiling hydrochloric acid, with evolution of hydrogen sulphide, while others are not dissolved by hydrochloric acid, but by concentrated and boiling nitric acid. The compounds of sulphur, with mercury, gold, and platinum, resist, more or less, the action of both acids, but dissolve in nitro-hydrochloric acid. Upon the solution of sulphides in nitric acid and in nitro-hydrochloric acid, sulphuric acid is formed, and in most cases sulphur is also separated. Many metallic sulphides, more especially those of a higher degree of sulphuration, give a sublimate of sulphur when heated in a tube closed at one end. All sulphides are decomposed by fusion with potassium nitrate and sodium carbonate; and on extracting the fusion with water, the sulphur is found in solution as sodium or potassium sulphate.

4. If hydrogen sulphide, in the gaseous state or in solution, is brought into contact with *silver nitrate* or *lead acetate*, black precipitates of SILVER SULPHIDE or LEAD SULPHIDE are formed. In cases, therefore, where the odor fails to afford sufficient proof of the presence of hydrogen sulphide, these reagents will remove all doubt. If the hydrogen sulphide is present in the gaseous form, the air suspected to contain it is tested by placing in it a small strip of paper moistened with solution of lead acetate and a little ammonia. If the gas is present, the paper becomes covered with a brownish-black, shining film of lead sulphide. To detect a trace of an alkali-metal sulphide in presence of a free alkali or an alkali carbonate, the best way is to mix the fluid with a solution of lead hydroxide in sodium hydroxide, which is prepared by mixing solution of lead acetate with sodium hydroxide solution until the precipitate which forms at first is redissolved.

5. If a fluid containing hydrogen sulphide or an alkali-metal sulphide is mixed with solution of sodium hydroxide, then with *sodium nitroprusside*, $Na_2Fe(NO)(CN)_5.2H_2O$, it acquires a fine reddish-violet tint. The reaction is very delicate; but that with solution of lead hydroxide in sodium hydroxide is still more sensitive.

6. Exceedingly minute traces of hydrogen sulphide in aqueous solution may be detected by adding $\frac{1}{50}$ of the volume of fuming hydrochloric acid and some small fragments of the sulphuric acid salt of *para-amido-dimethyl aniline*,* and also, as soon as the latter has dissolved, one or two drops of a dilute ferric chloride solution. In the presence of hydrogen sulphide, the liquid takes on a pure blue color in consequence of the formation of METHYLENE BLUE (H. CARO, E. FISCHER).

7. If metallic sulphides are exposed to the *oxidizing flame of the blowpipe*, the sulphur burns with a blue flame, emitting at the same time the well-known odor of SULPHUR DIOXIDE. If a sulphide is heated in a glass tube open at both ends, in the upper part of which a strip of moist, blue litmus-paper is inserted, and the tube is held in a slanting position during the operation, the escaping sulphur dioxide reddens the litmus-paper.

* Concerning the preparation of this reagent, see Zeitschr. f. analyt. Chem. 23, 226.

8. If a finely pulverized metallic sulphide is boiled in a porcelain dish with solution of potassium hydroxide, and the mixture heated to incipient fusion of the caustic potash, or if the substance to be tested is fused in a platinum spoon with caustic potash, and the mass is in either case dissolved in a little water, a piece of bright silver (a polished coin) put into the solution, and the fluid is warmed, a brownish-black film of SILVER SULPHIDE forms on the metal. This film may be removed afterwards by rubbing the metal with leather and quicklime (v. KOBELL).

9. If the powder of a sulphide which is decomposed by hydrochloric acid with difficulty or not at all, is mixed in a small cylinder or in a wide-necked flask, with an equal volume of finely divided iron free from sulphur (ferrum alcoholisatum), and some moderately dilute hydrochloric acid (1 volume of concentrated acid to 1 volume of water) is poured over the mixture, in a layer a few millimeters thick, HYDROGEN SULPHIDE escapes along with the hydrogen. This may be easily detected by placing a strip of paper moistened with solution of lead acetate and dried again, under the cork, so that the bottom is covered by it, the ends of the strip projecting on both sides, and then loosely inserting the cork into the mouth of the flask. Realgar, orpiment, and molybdenite do not show this reaction (v. KOBELL).

10. In relation to the microscopic detection of sulphur, see HAUSHOFER, p. 115; BEHRENS, Zeitschr. f. analyt. Chem., **30**, 166; F. EMICH, *ibid.*, **32**, 163.

§ 188.

Recapitulation and Remarks.—Most of the acids of the first group are also precipitated by silver nitrate, but the precipitates cannot well be confounded with the silver compounds of the acids of the second group, since the former are soluble in dilute nitric acid, while the latter are insoluble in that acid. The presence of hydrogen sulphide interferes more or less with the tests for the other acids of the second group. This acid must therefore, if present, be removed before the testing for the other acids can be proceeded with. The removal of

hydrosulphuric acid, when present in the free state and when cyanogen compounds are not also present, may be effected by simple ebullition. In other cases, it is best accomplished by the addition of a solution of zinc sulphate which has been treated with an excess of sodium or potassium hydroxide, and filtering off the zinc sulphide [or by the addition of cadmium sulphate solution to neutral, acid, or alkaline liquids, and filtering off the cadmium sulphide, which filters better than zinc sulphide]. Mixtures of insoluble metallic sulphides with insoluble chlorine, bromine, or iodine compounds may be prepared for analysis by fusing with sodium carbonate and potassium nitrate. When the mass is treated with carbonic acid water, heated, and filtered, the filtrate contains the sulphur as sulphate, while the chlorine, bromine, and iodine are combined with the alkali metals. The two latter may, however, be present partly as alkali bromate and iodate, but if the solution is acidified with dilute sulphuric acid and sulphurous acid is added in slight excess, it then contains only hydrochloric, hydrobromic, and hydriodic acids.

Hydrocyanic acid can be recognized, even in the presence of hydrochloric, hydrobromic, and hydriodic acids, by the reaction with ferrous-ferric solution, which is as delicate as it is characteristic. In the presence of alkali-metal ferro- and ferricyanides as well as sulphocyanides, a metallic cyanide may be detected by subjecting the liquid to distillation with the addition of hydrogen sodium carbonate. The cyanogen of cyanides is then found as hydrocyanic acid in the distillate. Ferrocyanogen and ferricyanogen may also be removed by careful precipitation by ferric or ferrous sulphate, respectively, and the cyanogen may be detected in the filtrate according to § 185, 6. The separation of ferrocyanogen from ferricyanogen, cyanogen, sulphocyanogen, chlorine, and bromine (but not from iodine), may be accomplished by treating the freshly precipitated silver compounds with aqueous ammonia, since silver ferrocyanide is insoluble in this liquid, while the other silver compounds dissolve in it. Silver ferrocyanide and also silver ferricyanide may be identified by the blue coloration which they show when they are moistened with sodium chloride solution and ferric chloride or ferrous sulphate solution, respectively.

Hydriodic acid may be readily detected in the presence of hydrogen chloride and bromide, with starch or carbon disulphide, upon the addition of a liquid containing nitrous acid. These iodine reactions may, however, be interfered with or prevented by the presence of cyanogen compounds, and, moreover, the detection of chlorine and bromine in the presence of iodine or cyanogen compounds is more or less difficult. Any cyanogen present must, therefore, be removed or rendered harmless before testing for iodine, and, furthermore, both cyanogen and iodine, if necessary, must be removed or rendered harmless before testing for bromine and chlorine. The removal of cyanogen, as well as ferrocyanogen, ferricyanogen, and sulphocyanogen, is accomplished by igniting all the silver compounds. Silver cyanide, ferrocyanide, ferricyanide, and sulphocyanide are decomposed (the latter with formation of silver sulphide), while silver chloride, bromide, and iodide suffer no decomposition. If, therefore, the ignited residue is fused with sodium and potassium carbonates, and the mass is boiled with water, sodium or potassium chloride, bromide, and iodide are obtained in solution. The fused silver compounds are also readily decomposed by metallic zinc. For this purpose, they are covered with water, a little dilute sulphuric acid is added and a fragment of zinc, the whole is allowed to stand for some time, and the resulting zinc chloride, bromide, and iodide solution is filtered from the separated metallic silver. If sulphocyanogen was present, hydrogen sulphide appears in this reduction, and this must be removed in the first place by boiling.

The separation of iodine from chlorine and bromine is effected by treating the silver compounds with ammonia, but more accurately by precipitating the iodine as cuprous iodide (§ 184, 6, first method). From bromine alone, iodine is separated most accurately by palladious chloride, which only precipitates the iodine; while from chlorine, it is separated by palladious nitrate, or, after the addition of a sufficient amount of ammonium sulphate, by means of thallous sulphate (P. Jannasch and K. Aschoff).

Bromine in presence of iodine and chlorine may be identified by the following simple operation: Mix the liquid with a few drops of dilute sulphuric acid, then with some starch paste, and

add a little red fuming nitric acid or, better still, a solution of nitrous acid in sulphuric acid, whereupon the iodine reaction shows itself immediately. Add now chlorine-water drop by drop until that reaction has disappeared; then add some more chlorine-water to set the bromine also free, which may then be separated and identified by means of chloroform or carbon disulphide. Or, the iodine after being liberated in a highly dilute fluid may be also taken up with chloroform or carbon disulphide, the aqueous fluid may then be filtered through a wet filter, and the bromine detected in the filtrate by means of chloroform or carbon disulphide and chlorine-water. For the latter process, the following may be substituted: Directly after the liberation of the iodine, cautiously add chlorine-water, when the violet-red coloration of the chloroform or carbon disulphide will gradually fade away, and give place to the brownish-yellow color indicative of bromine.

For the detection of chlorine, iodine, and bromine, in the presence of each other, the fresh precipitate of silver chloride, bromide, and iodide, washed by decantation is heated from two to three minutes to boiling with 80 to 100 parts by weight of an aqueous solution of ammonium sesqui-carbonate (see § 182,4, foot-note), it is allowed to stand a short time, the liquid is decanted, and the boiling with the ammonium carbonate is repeated with more of that solution. The solution contains the silver chloride (together with a trace of silver bromide). If the residual silver iodide and bromide is treated with 5 per cent ammonia-water (.9783 sp. gr.), the silver bromide dissolves (with traces of silver iodide), while almost the whole amount of the silver iodide remains behind (H. Hager). The precipitates thrown down by nitric acid from the ammoniacal solutions and the silver iodide remaining undissolved may then be fused with sodium carbonate, the fusions treated with water, and the filtrates, each of which now contains a halogen in an almost pure condition, may be subjected to further tests. For the detection of chlorine, the solution is neutralized with sulphuric acid (the reaction may be still somewhat alkaline, but must not be acid), it is evaporated to dryness, the residue is melted together with potassium dichromate, and the resulting mass is treated acording to § 182, 7. [The moist silver salts may be decomposed also very readily by agitating them with a little dilute

sulphuric acid and metallic zinc until they have become thoroughly black from their conversion into metallic silver. The filtrates may be directly subjected to further tests for iodine and bromine, but before evaporating the solution, sufficient sodium carbonate solution should be added to it to produce a permanent precipitate of basic zinc carbonate.]

The following method for the detection of small amounts of chlorine in the presence of iodine and bromine is similar in principle: Treat the completely washed silver precipitate for a few minutes in the cold with four or five volumes of a 10 to 15 per cent solution of ammonium sesqui-carbonate, allow it to settle, filter, and add potassium bromide to the filtrate. The formation of a precipitate shows the presence of silver which has gone into solution as silver chloride, and consequently the presence of chlorine. If iodates or cyanides were present, it would have been necessary to destroy them in the first place (L. L. DE KONINCK).

Chlorine may also be detected in the presence of bromine and iodine in the following way: Heat the solution, in which the halogens are presumed to be combined with alkali or alkali-earth metals, with lead dioxide and acetic acid, until the liquid is colorless after settling, and has no longer the slightest odor of iodine or bromine. In this operation, the bromine escapes with a part of the iodine, while the rest of the latter remains as lead iodate with the lead dioxide added in excess. Filter, wash the precipitate with hot water, and precipitate the chlorine from the filtrate with silver solution (G. VORTMANN).

After a great amount of experience, it is possible to detect chlorine, bromine, and iodine in the presence of each other by spectrum analysis, according to AL. MITSCHERLICH (compare Zeitschr. f. analyt. Chem., **4**, 153).

As regards the starch reaction, it should be noted that many salts (alum, alkali sulphates, magnesium sulphate, etc.) diminish its delicacy; and also, in regard to this and the carbon disulphide reaction, that many organic substances may entirely prevent their appearance, *e.g.*, albuminoids (PUCHOT), resorcin, orcin, phloroglucin (HLASIWETZ), and especially tannin. The fact should also be mentioned that when nitrous acid is used for the liberation of iodine in the presence of sul-

add a little red fuming nitric acid or, better still, a solution of nitrous acid in sulphuric acid, whereupon the iodine reaction shows itself immediately. Add now chlorine-water drop by drop until that reaction has disappeared; then add some more chlorine-water to set the bromine also free, which may then be separated and identified by means of chloroform or carbon disulphide. Or, the iodine after being liberated in a highly dilute fluid may be also taken up with chloroform or carbon disulphide, the aqueous fluid may then be filtered through a wet filter, and the bromine detected in the filtrate by means of chloroform or carbon disulphide and chlorine-water. For the latter process, the following may be substituted: Directly after the liberation of the iodine, cautiously add chlorine-water, when the violet-red coloration of the chloroform or carbon disulphide will gradually fade away, and give place to the brownish-yellow color indicative of bromine.

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sulphuric acid and metallic zinc until they have become thoroughly black from their conversion into metallic silver. The filtrates may be directly subjected to further tests for iodine and bromine, but before evaporating the solution, sufficient sodium carbonate solution should be added to it to produce a permanent precipitate of basic zinc carbonate.]

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After a great amount of experience, it is possible to detect chlorine, bromine, and iodine in the presence of each other by spectrum analysis, according to AL. MITSCHERLICH (compare Zeitschr. f. analyt. Chem., **4**, 153).

As regards the starch reaction, it should be noted that many salts (alum, alkali sulphates, magnesium sulphate, etc.) diminish its delicacy; and also, in regard to this and the carbon disulphide reaction, that many organic substances may entirely prevent their appearance, *e.g.*, albuminoids (PUCHOT), resorcin, orcin, phloroglucin (HLASIWETZ), and especially tannin. The fact should also be mentioned that when nitrous acid is used for the liberation of iodine in the presence of sul-

phocyanides, mistakes may occur (NADLER), because the fluid then assumes a reddish color, even in the absence of iodine, from the formation of pseudo-sulphocyanogen. Upon shaking with carbon disulphide, the greater part of the colored substance is taken up by this solvent.

As far as the agents for setting iodine free are concerned, many others have been proposed besides those mentioned above, *e.g.*, iodic acid, or an alkali-metal iodate and hydrochloric acid (v. LIEBIG), ferric chloride and sulphuric acid, platinic chloride with the addition of some hydrochloric acid (HEMPEL), potassium permanganate or chromic acid in slightly acidified solution, etc. In respect to these agents, it should be observed that iodic acid must be used with the greatest caution; in the first place, because in presence of reducing substances, iodine is set free from the reagent, and in the second place, an excess of iodic acid will at once put an end to the reaction. Ferric chloride, with addition of sulphuric acid, will not act immediately upon very dilute solutions; but after a time, the reaction will make its appearance, revealing the presence of even the minutest trace of iodine; and the delicacy of the reaction is not materially impaired by an excess of the reagent. Ferric chloride may be used with advantage when iodine is to be liberated in the gaseous state, which should be done, for example, in the presence of organic substances which prevent the iodized starch reaction, and when sulphocyanides are present. For this purpose, the liquid is heated nearly to boiling, and the escaping fumes are allowed to act on paper smeared with fresh starch paste. If a solution of ferric sulphate is used instead of ferric chloride, the residue may be used afterwards for testing for bromine and chlorine. If this is heated after the addition of potassium permanganate, the bromine escapes and is conveniently collected in some chloroform (HART), so that the residue now remaining, after reduction of the potassium permanganate by alcohol, may be tested for chlorine by means of silver solution. Where potassium permanganate is used for the liberation of iodine, if the reaction of starch solution with iodine is used, a conclusion concerning it ought not to be made until from six to twelve hours have elapsed, because a liquid colored with a little iodized starch may also appear reddish, and therefore may be confused with the coloration produced by perman-

ganic acid alone. The *modus operandi* may of course be modified in various ways to increase the delicacy of the starch reaction, and interesting particulars upon this point may be found in the papers of MORIN * and HEMPEL.†

For the distinction of the polysulphides of the alkali and alkali-earth metals from their normal sulphides, the following reaction will serve, in addition to the one given in § 187, 3: Heat pure 96 per cent alcohol in a flask to boiling, with the addition of some pieces of glass in order to regulate this, and, after the alcohol vapor has expelled the air, add the liquid to be tested drop by drop. If this contains a polysulphide, the liquid transiently assumes a sky-blue color, which changes into a permanent greenish-blue (J. C. GILL).‡

§ 189.

Rarer Acids of the Second Group.

1. NITROUS ACID, HNO_2. (*Nitrous Anhydride*, N_2O_3.)

NITROUS ANHYDRIDE forms a brownish-red gas at the ordinary temperature. In contact with water, it decomposes, mostly at least, into nitric acid, which dissolves, and nitric oxide, which partly escapes if the amount of water is not very large: $3N_2O_3 + H_2O = 2HNO_3 + 2N_2O_2$. The nitrites are decomposed by ignition, and most of them are soluble in water. If the salts or their concentrated solutions are treated with dilute sulphuric acid, nitrous anhydride is not evolved, but nitric oxide is, while at the same time nitric

* Journ. f. prakt. Chem., 78, 1.

† Annal. d. Chem. u. Pharm., 107, 102.

‡ Concerning further reactions for the detection of small amounts of hydrogen sulphide, compare CURTMAN, Zeitschr. f. analyt. Chem., 25, 561; ITALLIE, Chem. Centralbl., 1891, II, 498. In relation to the detection of small amounts of a chloride in the presence of much iodide, compare DIETZELL, Zeitschr. f. analyt. Chem., 8, 453; small amounts of bromine in presence of chlorine, BERGLUND, *ibid.*, 24, 184; small amounts of chlorine or bromine beside much iodine, BOHLIG, *ibid.*, 9, 315; small amounts of iodine in bromine and bromides, JORISSEN, *ibid.*, 19, 353; of chlorine, bromine, and iodine in presence of each other, DECHAN, *ibid.*, 28, 705; JONES, Pharmac. Centralhalle, 1884, p. 183; MACNAIR, *ibid.*, 1893, p. 519; HAGER, Chem. Centralbl., 1885, p. 315; F. KEBLER, *ibid.*, 1893, I, 365; of chlorine, bromine, iodine, cyanogen, ferro- and ferricyanogen, also of chloric, bromic, and iodic acids, as well as hydrogen sulphide in mixtures of all of them, LONGI, Zeitschr. f. analyt Chem., 23, 70; WELLS and VULTE, Pharmac. Centralhalle, 1890, p. 118.

acid is formed. Very dilute solutions of nitrites (*e.g.*, such as contain .006 g or less of nitrous acid per liter), when acidified with dilute sulphuric or acetic acid, and distilled, give, on the other hand, a distillate which contains almost the whole amount of the nitrous acid originally present, and, in fact, the first 10 or 20 cc which go over contain the greater part of it. This gives a means of obtaining the nitrous acid in a small volume of liquid, and at the same time of separating it from substances which might prevent its detection. It is self-evident that this method is not applicable when substances which decompose nitrous acid (*e.g.*, hydrogen sulphide) are present. In solutions of alkali nitrites, *silver nitrate* produces a white precipitate, which dissolves in a very large proportion of water, especially upon application of heat. *Ferrous sulphate* produces in neutral solutions a faint brownish-yellow coloration, but upon the addition of acetic acid, a deep blackish-brown coloration results, due to the solution of nitric oxide in the ferrous sulphate solution (difference from nitric acid). *Hydrogen sulphide* gives at once in solutions containing free nitrous acid, and gradually in solutions of normal alkali-metal nitrites, a white precipitate of separated sulphur. *Pyrogallic acid* imparts a brown color to even very dilute solutions of nitrites acidified with sulphuric acid (SCHÖNBEIN). On addition of *potassium cyanide* solution to an alkaline nitrite, then of some neutral solution of *cobalt chloride* and a little acetic acid, the fluid becomes orange-rose colored from the formation of potassium cobalt nitrocyanide (C. D. BRAUN). But a far more delicate reagent for nitrous acid is solution of *potassium iodide* or *zinc iodide** mixed with *starch paste*, especially upon addition of sulphuric acid (PRICE, SCHÖNBEIN). Water containing one hundred-thousandth part of potassium nitrite, together with free sulphuric acid, is colored distinctly blue by this reagent in a few seconds, and a few minutes suffice to produce the same effect in water containing one millionth part of potassium nitrite. This reaction is trustworthy, only where no other substance is present that might exercise a decomposing action upon potassium iodide, such as iodic acid, ferric salts, etc. In order to exclude the detrimental action of such substances, and to increase the delicacy of the reaction, about 300 cc of the water to be tested are distilled, with the addition of a little acetic acid, and the first drops going over are collected in a solution of an iodide and starch paste acidified with sulphuric acid. If a liquid containing nitrous acid is mixed with a colorless solution of *metadiamidobenzol (metaphenylene diamine)* in an excess of dilute sulphuric acid,† there is produced,

* A stable zinc iodide solution may be obtained according to the following directions 5 g of starch and 20 g of zinc chloride are boiled with about 100 cc of distilled water, the evaporated water being replaced, until the crusts of starch are almost completely dissolved; then 2 g of dry zinc iodide are added, the solution is diluted to 1 liter, and filtered. The solution should be preserved in well-closed bottles in the dark.

† The solution is decolorized with animal charcoal, and is then stable for months in closed bottles.

even in exceedingly dilute solutions, a characteristic yellow coloration (P. GRIESS). If a solution of *sulphanilic acid* in acetic acid, mixed with a colorless solution of *naphthylamine* in acetic acid,* is added to a liquid containing nitrous acid, and it is heated to 70° or 80°, there is produced in concentrated solutions a red coloration, which rapidly changes to yellow, while in dilute solutions a permanent rose-red color is produced (P. GRIESS, L. ILOSVAY, LUNGE). On adding *indigo solution* to water till the latter has lost its transparency from the depth of color, then hydrochloric acid, and afterwards a solution of *alkali-metal polysulphide* with stirring, till the blue color just vanishes, filtering and adding to the clear filtrate a solution of the merest trace of nitrous acid, a most distinct, bluish coloration will at once be produced. This reaction is to be recommended in the presence of other reducing bodies which interfere with the action of nitrous acid upon an acidified solution of starch and potassium iodide (SCHÖNBEIN). But it must not be overlooked that other oxidizing substances reproduce the blue color. On mixing a solution of nitrous acid (for instance, a solution of potassium nitrite acidified with acetic acid) with *potassium sulphocyanide*, the fluid is not colored, but on the addition of nitric acid, hydrochloric acid, or sulphuric acid, a dark-red color makes its appearance, which vanishes on addition of alcohol, or after heating for a short time (difference from ferric sulphocyanide). The coloring substance is mostly taken up by shaking with carbon disulphide. The following reaction is especially adapted for the detection of nitrous acid in concentrated sulphuric acid: A trace of resorcin is added to 1 cc of the acid, and it is then diluted with 5 cc of water and shaken. The slightest trace of nitrous acid may be thus detected by a yellow coloration (WILSON). *Potassium permanganate* does not act upon neutral solutions of nitrites, but upon the addition of a dilute acid, decoloration takes place, and in the presence of an excess of permanganic acid, all the nitrous acid is converted into nitric acid. *Hydrogen peroxide* also rapidly oxidizes nitrous acid in acid solution to nitric acid (WILFRATH, SCHÖNE).† Concerning the

* .5 g of sulphanilic acid is dissolved in 150 cc of acetic acid; .1 g of solid naphthylamine is boiled with 20 cc of water, the colorless solution is poured off from the bluish-violet residue and mixed with 150 cc of acetic acid The two solutions are mixed, decolorized, if necessary, by shaking with zinc dust, and the reagent is preserved in well-closed bottles.

† Other means of detecting minute, or exceedingly minute, amounts of nitrous acid are diamidobenzoic acid, P. GRIESS, Zeitschr. f. analyt. Chem., 10, 93; diphenylamine, E. KOPP, *ibid.*, 11, 461; carbolic acid and mercurous nitrate, P. C. PLUGGE, *ibid.*, 14, 131; fuchsine, A. JORISSEN, *ibid.*, 21, 210; para-amidobenzolazodimethyl aniline, MELDOLA, Ber. d. deutsch. chem. Gesellsch., 17, 256; Zeitschr. f. analyt. Chem., 24, 98; gallic acid, DAVY, Zeitschr. f. analyt. Chem., 23, 72; antipyrine, CURTMAN, *ibid.*, 29, 194; sulphanilic acid and phenol, P. F. FRANKLAND, *ibid.*, 30, 713; potassium ferrocyanide and acetic acid, SCHEFFER, DEVENTER, Ber. d. deutsch. chem. Gesellsch., 1893, p. 589. Many reactions of nitrous acid may be confused

microscopic detection of nitrous acid, see BEHRENS, Zeitschr. f. analyt. Chem., 30, 165.

§ 190.

2. HYPOCHLOROUS ACID, HClO. (*Hypochlorous Oxide*, Cl_2O.)

HYPOCHLOROUS OXIDE, Cl_2O, at the common temperature, is a deep yellow gas of a disagreeable, irritating odor, similar to that of chlorine. It explodes upon heating, decomposing into chlorine and oxygen. It dissolves in water, and the dilute aqueous solution bears distillation. The hypochlorites usually occur mixed with metallic chlorides, as is the case, for instance, in chloride of lime, *eau de Javelle*, etc. The solutions of hypochlorites undergo alteration by boiling, the hypochlorite being resolved into chloride and chlorate, attended in the case of concentrated, but not in that of dilute solutions, with evolution of oxygen. If a solution of chloride of lime is mixed with hydrochloric acid or sulphuric acid in excess, chlorine is disengaged, while hypochlorous acid is set free by passing carbonic acid into it. *Silver nitrate* throws down silver chloride from a solution of chloride of lime which has been so far neutralized with nitric acid that it does not yet give an odor of chlorine. The silver hypochlorite which is transiently formed, decomposes very soon into silver chloride and chlorate: $3AgClO = AgClO_3 + 2AgCl$. *Lead nitrate* produces a precipitate which from its original white color changes gradually to orange-red, and ultimately, owing to formation of lead dioxide, to brown. *Manganese salts* give brownish-black precipitates of hydrated manganese dioxide. Free hypochlorous acid, acting upon *mercury*, produces yellowish-brown mercuric oxychloride (while chlorine gives mercurous chloride). If so little hypochlorous acid is present, with much chlorine, that the color of the precipitate cannot be certainly recognized after the shaking, the precipitate resulting after long shaking is treated with hydrochloric acid (which dissolves the oxychloride, but leaves the mercurous chloride unchanged), this is filtered, and hypochlorous acid is recognized by the presence of mercuric chloride in the filtrate. Hypochlorites may be detected even more easily than the free acid by shaking their solutions with mercury, because in their presence mercuric oxide is formed, yellow in color and gradually becoming red, which adheres to the surface of

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with those of *ozone* and *hydrogen peroxide*, and in relation to those by which they may be distinguished (since this subject does not admit of being sufficiently explained in a concise manner), I will refer to the treatises of EM. SCHÖNE, Ber. d. deutsch. chem. Gesellsch., 7, 1698; 11, 482, 561, 874, 1028; Zeitschr. f. analyt. Chem., 18, 133; and above all, to the one most recently published, *ibid.*, 33, 137, in which the work of other investigators upon this subject is referred to and discussed.

the glass upon shaking. Chlorous and chloric acids, when they are combined with bases, do not attack mercury (WOLTERS). Solution of *potassium permanganate* is not decolorized. Solutions of *litmus* and *indigo* are decolorized somewhat by alkaline solutions of hypochlorites, but far more rapidly and completely upon addition of an acid. If a solution of arsenious oxide in hydrochloric acid is colored blue with solution of indigo, and a solution of chloride of lime is added, with active stirring, the decoloration will take place only after the whole of the arsenious oxide has been converted to arsenic acid.

§ 191.

3. CHLOROUS ACID, $HClO_2$. (*Chlorous Oxide*, Cl_2O_3.)

CHLOROUS OXIDE, Cl_2O_3, is a yellowish-green gas of a peculiar and very disagreeable odor. It explodes at 57°, and is thereby converted into chlorine and oxygen. It is soluble in water, and the solution has an intensely yellow color, even when highly dilute. Most of the chlorites are soluble in water, and the solutions readily suffer decomposition, the chlorites being resolved into chlorides and chlorates. *Silver nitrate* precipitates white silver chlorite, which is soluble in much water. A solution of *potassium permanganate* is immediately decomposed by free chlorous acid, and a brown precipitate separates after some time. *Tincture of litmus* and *solution of indigo* are instantly decolorized, even if mixed with arsenious acid in excess. If a slightly acidified, dilute solution of a *ferrous salt* is mixed with a dilute solution of chlorous acid, the fluid transiently acquires an amethyst tint, and not until after the lapse of a few seconds, assumes the yellowish coloration of ferric salts (LENSSEN).

§ 192.

4. HYPOPHOSPHOROUS ACID, H_3PO_2.

The concentrated solution of hypophosphorous acid is of a syrupy consistence, and resembles that of phosphorous acid (see § 178), with which it also has this in common, that it is resolved by heating, with exclusion of air, into phosphoric acid and hydrogen phosphide gas which is not spontaneously inflammable. Almost all hypophosphites are soluble in water; and by ignition, all of them are resolved into phosphates, and hydrogen phosphide which in most cases is spontaneously inflammable, and a portion of which decomposes into phosphorus and hydrogen. *Barium chloride*, *calcium chloride*, and *lead acetate* fail to precipitate solutions of hypophosphites (difference from phosphorous acid). *Silver nitrate* gives at first with hypophosphites a white precipitate of silver hypophosphite, which turns black even at the common temperature, but more rapidly on heating, the

change of color being attended with separation of metallic silver. From excess of *mercuric chloride*, hypophosphorous acid precipitates mercurous chloride slowly in the cold, but more rapidly on heating. If the nitric acid solution of *ammonium molybdate* (§ 55) is mixed with a liquid containing hypophosphorous acid, and a few drops of aqueous sulphurous acid are added, upon warming gently, a blue precipitate or a fine blue coloration is produced. Hydrogen sulphide, thiosulphates, chlorates, as well as stannous chloride, prevent the appearance of this very delicate reaction (MILLARD). A solution of *copper sulphate* gives with hypophosphorous acid, and also with its salts, upon heating, a reddish-brown precipitate of cuprous hydride, Cu_2H_2 (WURTZ). When brought together with *zinc* and *dilute sulphuric acid*, hypophosphorous acid gives hydrogen containing hydrogen phosphide (compare phosphorous acid, § 178).

Third Group of Inorganic Acids.

ACIDS WHICH ARE NOT PRECIPITATED BY BARIUM SALTS NOR BY SILVER SALTS: *Nitric Acid*, *Chloric Acid* (Perchloric Acid).

§ 193.

a. NITRIC ACID, HNO_3. (*Nitric Anhydride*, N_2O_5.)

1. NITRIC ANHYDRIDE crystallizes in six-sided prisms. It fuses at 29.5°, and boils at about 45° (DEVILLE). NITRIC ACID, HNO_3, is a colorless (red when it contains nitrogen peroxide), exceedingly corrosive fluid, which emits fumes in the air, exercises a rapidly destructive action upon organic substances, and colors many nitrogenous matters intensely yellow. It boils at 86°, and has a specific gravity of 1.522.

2. The NORMAL SALTS of nitric acid, with few exceptions (cinchonamine, ARNAUD and PADE), are soluble in water, but some of the basic nitrates are insoluble. All nitrates undergo decomposition at an intense red heat. Nitrates of the alkali metals at first yield oxygen, and change to nitrites; but afterwards they yield oxygen and nitrogen. Some others yield oxygen and nitrogen peroxide, while many (containing water) give off nitric acid.

3. If a nitrate is thrown upon *red-hot charcoal*, or if charcoal or some organic substance, paper for instance, is brought

into contact with a nitrate in fusion, DEFLAGRATION takes place, *i.e.*, the charcoal burns at the expense of the oxygen of the nitric acid, with vivid scintillation.

4. If a mixture of a nitrate with *potassium cyanide* in powder is heated on platinum foil, a vivid DEFLAGRATION ensues, attended with distinct ignition and detonation. *Very small quantities* only should be used for this experiment.

5. If a nitrate is mixed with *copper filings*, and the mixture heated in a test-tube with concentrated sulphuric acid, the air in the tube acquires a yellowish-red tint, owing to the nitric oxide gas which is liberated upon the oxidation of the copper by the nitric acid, combining with the oxygen of the air to form nitrogen peroxide. The coloration may be observed most distinctly by looking lengthwise through the tube.

6. If the solution of a nitrate is mixed with an equal volume of concentrated *sulphuric acid*, free from nitric and nitrous acids, the mixture allowed to cool, and a concentrated solution of *ferrous sulphate* then cautiously added to it, so that the fluids do not mix, the junction shows at first a purple, afterwards a brown color, or, in cases where only a very minute quantity of nitric acid is present, a reddish color. On mixing the fluids a little, the brown zone becomes wider. The nitric acid is decomposed by the ferrous salt, three fifths of the oxygen of nitric anhydride oxidizing a part of the ferrous sulphate to ferric sulphate, while the nitric oxide, NO, thus formed, combines with more of the ferrous sulphate to form a peculiar compound which dissolves in water with a brownish-black color. Considerable amounts of chlorides interfere with the delicacy of the reaction. A similar reaction is observed in presence of selenious acid; but on mixing the fluid and letting it stand, red selenium separates (WITTSTOCK).

7. If a little hydrochloric acid is boiled in a test-tube, one or two drops of very dilute solution of *indigo in sulphuric acid* are added, and the mixture is again boiled, the liquid remains blue (if the hydrochloric acid was free from chlorine). If a nitrate, either solid or dissolved, is now added to the faintly light blue solution and it is again boiled, the liquid is decolorized on account of the destruction of the indigo. The addition of sodium chloride increases the delicacy of this (in its simple form) very delicate reaction. It must be borne in

mind, however, that several other oxidizing agents, especially free chlorine, also cause decoloration of solution of indigo.

8. If a little *brucine* is dissolved in a porcelain dish or upon a watch-glass, in pure concentrated sulphuric acid,* and a drop of a fluid containing nitric acid added to the edge of the solution, the latter immediately acquires a magnificent red color at the place of contact. This reaction is extraordinarily delicate. The bright red color soon passes into reddish-yellow. Chloric acid gives a similar reaction.

9. If 1 part of *phenol* (*carbolic acid*) is dissolved in 4 parts of concentrated sulphuric acid, and 2 parts of water are added, and a drop or two of this fluid added to a solid nitrate (*e.g.*, to the residue obtained by evaporating a small amount of well-water containing nitrates), a reddish-brown color is produced, from the formation of a nitro-compound of phenol. On addition of a drop or two of strong ammonia, this color turns yellow, sometimes passing through a green shade. This is a very delicate reaction (H. SPRENGEL). It may also be carried out by adding one or two drops of the liquid to be tested to some pure concentrated sulphuric acid, then adding a crystal of phenol and warming a little; and also by acidifying the liquid to be tested for nitric acid strongly with hydrochloric acid, adding a little phenol, and heating to about 80° or 90°. In the presence of nitric acid, a dark coloration always takes place, which is generally red or brown, but under certain conditions is green (H. HAGER).

10. If a little pure concentrated sulphuric acid is poured over a few crystals of *diphenylamine*, a little water is added, and the resulting solution is mixed with more concentrated sulphuric acid, an excellent reagent for nitric acid is obtained, which is best adapted for the detection of very small quantities when it contains only 1 mg of diphenylamine in 10 cc. If only about .5 cc of this solution are placed upon a watch-glass or the inverted cover of a porcelain crucible, and a drop of the liquid to be tested for nitric acid is allowed to

* In consequence of containing a small quantity of oxides of nitrogen, the common, pure concentrated sulphuric acid of commerce usually gives, with brucine alone, a rose-red coloration. But such an acid may be easily purified by diluting it with water to a specific gravity of 1.4, and heating it to boiling for a long time, best in a platinum dish.

fall into the middle of the reagent, there is formed, to the extent to which the liquids mix, a ring of a magnificent blue color (E. KOPP). This very delicate reaction may also be carried out by adding a few drops of the sulphuric acid salt of diphenylamine to the liquid to be tested for nitric acid, then adding pure concentrated sulphuric acid in such a manner that two layers are formed. The blue colorations gradually change to green, and finally disappear. The interpretation of the reactions requires caution, since many other substances also give a blue coloration, *e.g.*, nitrous, chloric, hypochlorous, bromic, iodic, vanadic, chromic, permanganic, and molybdic acids, and also ferric salts, hydrogen peroxide, and barium peroxide (LAAR).

11. If a few drops of sulphate of *paratoluidine* solution are added to the solution of a nitrate, and then an equal volume of concentrated sulphuric acid, with the precaution that the liquids do not mix, there appears at once at the surface of contact of the two liquids a red zone, the color of which slowly changes to dark yellow.* The reaction is not as delicate as those given by brucine or diphenylamine, but, on the other hand, it is adapted for the detection of nitric acid in the presence of small quantities of nitrous acid, since the latter produces at first a yellowish or yellowish-brown coloration, which changes to red only after some time (LONGI). Chloric acid and other oxidizing agents yield similar colorations.

12. Very minute quantities of nitric acid may be detected, also, by first reducing the nitric acid to nitrous acid, which may be effected both in the wet and in the dry way; in the former, by heating the solution of the nitric acid or of the nitrate for some time with finely divided zinc, best with zinc amalgam, and then filtering (SCHÖNBEIN); in the dry way, by fusing the substance with sodium carbonate at a moderate heat, extracting the mass, after cooling, with water, and filtering. Upon adding either of the filtrates to a solution of

* The reaction may be also produced with a sulphuric acid solution of an aniline oil which contains aniline and paratolnidine. C. D. BRAUN recommended such a solution as early as 1867 (Zeitschr. f. analyt. Chem., 6, 72). The manner of carrying out the operation, as recommended by him, varies somewhat from that given by LONGI.

potassium iodide mixed with starch paste and pure dilute sulphuric acid, the fluid acquires a blue color from iodized starch (compare § 189).

13. If a nitrate is brought into a solution of potassium hydroxide, and some aluminium or some zinc and iron filings are added, ammonia is set free upon gentle heating, and this may be readily detected by § 96, 3 or 4. Of course, nitrous acid gives the same reaction.

14. In relation to the microscopic detection of nitrates, see HAUSHOFER, p. 115; BEHRENS, Zeitschr. f. analyt. Chem., **30**, 165.

§ 194.

b. CHLORIC ACID, $HClO_3$.

1. CHLORIC ACID, in its most highly concentrated solution, is a colorless or slightly yellowish fluid, having a faint odor resembling that of nitric acid. It first reddens litmus, then bleaches it. Dilute chloric acid is colorless and odorless.

2. All CHLORATES are soluble in water. When they are heated to redness, either the whole of the oxygen escapes and metallic chlorides remain, or chlorine and the oxygen of the chloric anhydride are evolved, while oxides remain behind (chlorates of the earth metals).

3. Heated with *charcoal* or some organic substance, the chlorates DEFLAGRATE, and with far greater violence than the nitrates.

4. If a mixture of a chlorate with *potassium cyanide* is heated on platinum foil, DEFLAGRATION takes place, attended with strong detonation and ignition, even though the chlorate is present only in minute quantity. This experiment should be made with very small quantities *and with great caution!*

5. If the solution of a chlorate is colored light blue with a sulphuric acid *solution of indigo*, a little dilute sulphuric acid added, and a solution of sodium sulphite dropped cautiously into the blue fluid, the color of the indigo disappears immediately. The cause of this equally characteristic and delicate reaction is, that the sulphurous acid deprives the chloric

acid of its oxygen, thus setting chlorine or a lower oxide of it free, which then decolorizes the indigo. An excess of sulphurous acid is evidently to be avoided, because otherwise hydrochloric and sulphuric acids are produced.

6. If chlorates are treated with moderately dilute *hydrochloric acid*, the constituents of the two acids transpose, especially upon heating, forming water, chlorine, and chlorine peroxide, ClO_2. In this process, the test-tube in which the experiment is made becomes filled with a greenish-yellow gas of a very disagreeable odor, resembling that of chlorine, while the hydrochloric acid acquires a greenish-yellow color. If the hydrochloric acid is colored blue with indigo solution, the presence of very minute quantities of chlorates will suffice to destroy the indigo color at once.

7. If a little chlorate is added to a few drops of *concentrated sulphuric acid* in a watch-glass, the liberated chloric acid breaks up into perchloric acid and chlorine peroxide: $3HClO_3 = HClO_4 + 2ClO_2 + H_2O$. Chlorine peroxide imparts an intensely yellow tint to the sulphuric acid, and betrays its presence also by its characteristic and very disagreeable odor. The application of heat must be avoided in this experiment, and the quantities operated upon should be very small, since otherwise the decomposition may take place with such violence as to cause a dangerous explosion, for the greenish-yellow chlorine peroxide explodes at as low a temperature as 60°.

8. If a drop of an aqueous solution of the sulphuric acid salt of aniline is added to the solution of a chlorate in concentrated sulphuric acid, prepared as in 7, a deep blue coloration of the liquid is produced, which is increased by adding a few drops of water. This is a very delicate reaction, which nitric acid does not give (VITALI).

9. Towards solutions of *brucine* (LUCK), *diphenylamine*, *paratoluidine*, and also *phenol* in concentrated sulphuric acid, chloric acid behaves like nitric acid, or at least so similarly that the two acids cannot be certainly distinguished by these reagents. On the other hand, chloric acid may be distinguished from nitric acid according to 8, as well as by *phenol* in hydrochloric acid solution (compare § 193, 9), since chloric acid produces in such a solution, according to circumstances, an orange-red turbidity or a transient yellow coloration.

10. If a dilute, aqueous solution of an alkali-metal chlorate is boiled with the *copper-zinc element** of GLADSTONE and TRIBE, complete reduction to alkali-metal chloride takes place, with separation of zinc oxide (THORPE and ECCLES). In solutions acidified by sulphuric acid, the chloric acid set free is converted into hydrochloric acid by the nascent hydrogen produced when *zinc* is added.

§ 195.

Recapitulation and Remarks.—Of the reactions which have been given to effect the detection of nitric acid, those with ferrous sulphate and sulphuric acid, with copper filings and sulphuric acid, and also those based upon the reduction to nitrites or to ammonia, give the most positive results. With regard to deflagration with charcoal, detonation with potassium cyanide, decoloration of solution of indigo, and the delicate reactions with brucine, diphenylamine, and paratoluidine, it has been shown that these reactions give no certain distinction, and are consequently decisive only where no chloric acid is present. The presence of *free nitric acid* in a fluid may be detected by evaporating it to dryness in a porcelain dish on the water-bath, having first thrown in a few white quill-cuttings. A yellow coloration of the latter shows the presence of nitric acid (RUNGE). The best way to ascertain whether or not CHLORIC ACID is present (in the absence of other oxygen compounds of chlorine) is to ignite the substance, with addition of sodium carbonate, dissolve the mass, and test the solution with silver nitrate. If a chlorate was present, this is converted into a chloride upon ignition, and silver nitrate produces a precipitate of silver chloride. However, the process is thus simple only if no chloride is present with the chlorate. In presence of a chloride, the chlorine of the latter must be removed by adding silver nitrate to the solution as long as a precipitate continues to form, and filtering; after addition of pure sodium carbonate, the filtrate is then evaporated and ignited.

* The copper-zinc element is obtained by treating thin sheet-zinc with 1 per cent copper sulphate solution, whereupon the zinc becomes black from precipitated copper. After washing and drying, the element is ready for use.

It is generally unnecessary, however, to pursue this circuitous way, since the reactions with concentrated sulphuric acid, with indigo and sulphurous acid, as well as with the sulphuric acid salt of aniline, are sufficiently marked and characteristic to afford positive proof of the presence of chloric acid, even in presence of nitrates. The best way of detecting nitric acid in presence of a large proportion of chloric acid is to mix the substance with sodium carbonate in excess, evaporate if necessary, ignite the residue moderately, but sufficiently long to convert the chlorate into chloride, and then test the residue for nitric acid, or for nitrous acid. If it is desired to detect nitric acid in the presence of nitrous acid, pure urea is added to the aqueous solution, and the liquid is slowly added to a solution of urea in dilute sulphuric acid. The decomposition of the nitrous acid then takes place at once, with the evolution of nitrogen and carbonic acid. If potassium iodide and dilute starch paste are added as soon as the reaction is finished, the liquid remains colorless. If a little finely divided zinc is now added, the blue coloration which appears (§193, 12) shows the presence of nitric acid (PICCINI).*

§ 196.

PERCHLORIC ACID, $HClO_4$.

The anhydride of perchloric acid is unknown. PERCHLORIC ACID forms a colorless, corrosive liquid, which gives dense fumes in the air, and decomposes with violent explosion after some time when kept, but at once when dropped upon charcoal, wood, or paper. The hydrate, $HClO_4.H_2O$, crystallizes in needles. The acid and the crystals dissolve in water with

* In regard to the detection of nitric acid in the presence of nitrous acid, see also LONGI, Zeitschr. f. analyt. Chem., 23, 352; concerning the detection of nitric acid in solutions containing iodides, bromides, chlorates, bromates, iodates, etc., see LONGI, *ibid.*, 23, 149; and in relation to the detection of chloric acid beside hydrochloric, hydrobromic, hydriodic, hydrocyanic, hydroferrocyanic and hydroferricyanic acids, and also bromic and iodic acids, see LONGI, *ibid.*, 23, 70. In regard to further means of detecting small quantities of nitric acid, see BRÉAL, Chem. Centralbl., 1888, p. 864; LINDO, *ibid.*, 1888, p. 1442; ROSENFELD, Zeitschr. f. analyt. Chem., 29, 661; v. UDRÁNSZKY, *ibid.*, 29, 732; and in relation to the detection of chloric acid in presence of nitric acid, see BÉHAL, Chem. Centralbl., 1886, p. 124.

the production of much heat. By distillation, the dilute solution gives first water, then dilute acid, and finally concentrated acid. All perchlorates are soluble in water, most of them freely. They are all decomposed by ignition, those with alkali bases leaving chlorides behind, with disengagement of oxygen. In not too dilute solutions, *potassium salts* produce a white, crystalline precipitate of potassium perchlorate, $KClO_4$, which is sparingly soluble in water, but insoluble in alcohol. *Barium salts* and *silver salts* are not precipitated. Concentrated sulphuric acid fails to decompose perchloric acid in the cold, and decomposes it with difficulty on heating (difference from chloric acid). Hydrochloric acid, nitric acid, and sulphurous acid fail to decompose aqueous solutions of perchloric acid or perchlorates; and therefore solution of indigo, previously added to it, is not decolorized (difference from all other acids of chlorine). Alkali-metal perchlorates are not reduced by the copper-zinc element (§ 194, 10, difference from chloric acid).

II. Organic Acids.

First Group.

The acids of the first group are decomposed partially or entirely by ignition;* also by boiling with concentrated nitric acid.† Their normal calcium salts are insoluble or difficultly soluble in water. The solutions of their normal alkali-metal salts are not precipitated nor colored by ferric chloride: OXALIC ACID, TARTARIC ACID (*racemic acid*), CITRIC ACID, MALIC ACID.

§ 197.

a. Oxalic Acid, $H_2C_2O_4$.

The reactions of this acid have already been given in § 175.

b. Tartaric Acid, $H_2C_4H_4O_6$.

1. Tartaric acid forms colorless crystals of an agreeable, acid taste, which are stable in the air, and soluble in water

* Oxalic acid, when cautiously heated, partially sublimes unaltered.

† The decomposition of oxalic acid by boiling nitric acid into carbon dioxide and water is slow.

and in alcohol. It is but slightly soluble in ether (.4 : 100, according to E. BOURGOIN). Heated to 100°, tartaric acid loses no water; heated to 170°, it fuses; while at a higher temperature, it becomes carbonized, emitting during the process a very peculiar and highly characteristic odor, which resembles that of burnt sugar. Aqueous solution of the commonly occurring tartaric acid, as also of almost all tartrates, turns the plane of polarization of light towards the right. There is, however, a left-rotating or lævo-tartaric acid, which, in its crystalline form, differs somewhat from the ordinary or dextro-tartaric acid, but otherwise both show the same reactions.

2. The TARTRATES of the alkali metals are soluble in water, as are some others, for example, aluminium and ferric tartrates. Evaporated on the water-bath to a syrupy consistence, the solution of ferric tartrate deposits a pulverulent basic salt. Those tartrates which are insoluble in water dissolve in hydrochloric or nitric acid. Many tartrates which are insoluble or difficultly soluble by themselves form with alkali-metal tartrates double salts, soluble in water. When heated to redness, the tartrates suffer decomposition, charcoal separates, and the same peculiar odor is emitted as attends the carbonization of the free acid.

3. If to a solution of tartaric acid, or to that of an alkali tartrate, solution of *an aluminium or a ferric salt* is added in not too large proportion, and then ammonia or potassium hydroxide, no precipitation of aluminium or ferric hydroxide takes place, since the double tartrates formed are not decomposed by alkalies. Tartaric acid also prevents the precipitation of several other hydroxides by alkalies (as do citric acid, malic acid, etc.).

4. Free tartaric acid produces with *potassium salts*—best with the acetate—a sparingly soluble precipitate of HYDROGEN POTASSIUM TARTRATE, $HKC_4H_4O_6$. The same precipitate is formed when potassium acetate and free acetic acid are added to the solution of the normal tartrate. Hydrogen potassium tartrate dissolves readily in alkalies and mineral acids; but tartaric and acetic acids do not increase its solubility in water. The separation of the hydrogen potassium tartrate precipitate is greatly promoted by shaking, or by

rubbing the sides of the vessel with a glass rod. In order that the reaction may be delicate, the tartaric acid solution should be very concentrated. The addition of an equal volume of alcohol heightens the delicacy of the reaction. In the presence of boric acid, the reaction appears only when potassium fluoride is used instead of potassium acetate, since this forms potassium borofluoride, and prevents the production of the very soluble compound containing boric acid, tartaric acid, and potassium (BARFOED).

5. From solutions of normal tartrates, *calcium chloride* added in excess * throws down a white precipitate of CALCIUM TARTRATE, $CaC_4H_4O_6.4H_2O$. Presence of ammonium salts retards the formation of this precipitate for a more or less considerable space of time. Agitation of the fluid or friction on the sides of the vessel promotes the separation of the precipitate. The precipitate is crystalline, or invariably becomes so after some time; and dissolves to a clear fluid in a cold, not too dilute solution of potassium or sodium hydroxide which is pretty free from carbonate. But upon boiling the solution, the dissolved calcium tartrate separates again in the form of a gelatinous precipitate, which redissolves upon cooling.

6. *Lime-water* added in excess * produces in solutions of normal tartrates—and also in a solution of free tartaric acid, if added to alkaline reaction—white precipitates which, while flocculent at first, assume afterwards a crystalline form. As long as they remain flocculent, they are readily dissolved by tartaric acid as well as by solution of ammonium chloride. From these solutions, the calcium tartrate separates again, after the lapse of several hours, in the form of small crystals deposited upon the sides of the vessel.

7. *Solution of calcium sulphate* added in excess * fails to produce a precipitate in a solution of tartaric acid; but in solutions of normal tartrates of the alkali metals, it produces a trifling precipitate after some time.

* Potassium or sodium tartrate dissolves calcium tartrate (as well as certain other salts insoluble in water, such as calcium phosphate, barium sulphate, etc.). Hence the alkali tartrate must be fully decomposed by the reagent before the reactions depending upon the separation of calcium tartrate can take place.

8. If solution of ammonia is poured upon even a very minute quantity of calcium tartrate, a small fragment of crystallized *silver nitrate* is added, and the mixture is slowly and gradually heated, the sides of the test-tube are covered with a bright coating of metallic silver. If, instead of a crystal, solution of silver nitrate is used, or heat is applied more rapidly, the reduced silver will separate in a pulverulent form (ARTHUR CASSELMANN).

9. *Lead acetate* produces white precipitates in solutions of tartaric acid and its salts. The washed precipitate, $PbC_4H_4O_6$, dissolves readily in nitric acid, and in ammonia free from carbonic acid.

10. *Silver nitrate* does not give a precipitate with free tartaric acid; but in solutions of normal tartrates, it produces a white precipitate of SILVER TARTRATE, $Ag_2C_4H_4O_6$, which dissolves readily in nitric acid and in ammonia. Upon boiling, it turns black, owing to reduced silver.

11. If there is added to a solution of free tartaric acid, or to that of an alkali-metal tartrate, a small quantity of *ferrous chloride* or *ferrous sulphate*, then one or two drops of *hydrogen peroxide* or some small particles of *sodium peroxide*, and finally an excess of sodium or potassium hydroxide solution, a beautiful violet coloration appears. The reaction is not very delicate, but it permits tartaric acid to be distinguished from citric, malic, and succinic acids (FENTON).

12. If tartaric acid or a tartrate is heated in a test-tube, with concentrated sulphuric acid, upon the water-bath, a browning of the sulphuric acid occurs almost simultaneously with the evolution of gas (difference from citric acid).

13. If a saturated solution of *potassium dichromate* is poured over a crystal of tartaric acid at the ordinary temperature, carbonic acid is given off, and the zone surrounding the tartaric acid crystal is colored purplish-violet to black (means of detecting tartaric acid in citric acid, for this is colored coffee-brown, and, in fact, very slowly, CAILLETET). This reaction may be carried out with an aqueous solution of tartaric acid. This is mixed with dilute sulphuric acid, one or two drops of a solution of potassium chromate are added, and it is heated for some time, whereupon the yellow color changes to the blue-violet of a chromic salt solution (SALZER).

14. If a weakly acid solution of *ammonium molybdate* is mixed with some tartaric acid, one or two drops of hydrogen peroxide, or a trace of sodium peroxide (but not more) are added, and it is gently warmed (60°), the original wine-yellow color changes through green to blue (CRISMER).

15. If there are added to some solid tartaric acid or to a tartrate a few drops of a solution of resorcin in concentrated sulphuric acid (about 1 : 100), and the mixture is warmed until sulphuric acid vapors just begin to escape, the liquid assumes a beautiful wine-red color. This reaction permits the detection of even the minutest quantities of tartaric acid (E. MOHLER).

16. Concerning the microscopic detection of tartaric acid, see HAUSHOFER, p. 85.

§ 198.

c. CITRIC ACID, $H_3C_6H_5O_7$.

1. Crystallized CITRIC ACID, obtained by the cooling of its solution, has the formula $C_6H_8O_7.H_2O$. It forms pellucid, colorless, and inodorous crystals of an agreeable, strongly acid taste, which dissolve readily in water and in alcohol, more difficultly in ether (2.26 : 100), and effloresce slowly in the air. When pulverized and heated gradually to 55°, the acid loses its water of crystallization (SALZER); when subjected to the action of a stronger heat, it fuses at first, and afterwards carbonizes, with evolution of pungent acid fumes, the odor of which may be readily distinguished from that emitted by tartaric acid upon carbonization. The aqueous solution of citric acid is optically inactive. By heating with moderately dilute nitric acid, in addition to nitro-compounds, oxalic and mesaconic acids are formed.

2. The CITRATES with alkali bases, whether normal or acid, are readily soluble in water, and therefore, solution of citric acid is not precipitated by potassium acetate. Various citrates containing weak bases, such as ferric citrate, are also freely soluble in water. Evaporated on the water-bath

to a syrupy consistence, the solution of ferric citrate deposits no solid salt. Citrates, like tartrates, and for the same reason, prevent the precipitation of aluminium and ferric hydroxides, etc., by alkalies.

3. *Calcium chloride* fails to produce a precipitate in solution of free citric acid, even upon boiling; but a precipitate of NORMAL CALCIUM CITRATE, $Ca_3(C_6H_5O_7)_2.4H_2O$, forms immediately upon saturating with potassium or sodium hydroxide, the somewhat concentrated solution of citric acid mixed with calcium chloride in equivalent amount or in slight excess.* The precipitate is insoluble in potassium or sodium hydroxide, readily soluble in alkali citrates, and rather more difficultly so in calcium chloride. It also dissolves freely in solution of ammonium chloride, and upon boiling this solution, if it is not prepared with too much ammonium chloride, normal calcium citrate separates again in the form of a white, crystalline precipitate, which, however, is now no longer soluble in ammonium chloride. If a solution of citric acid mixed with calcium chloride, as described above, is saturated with ammonia, or if ammonium chloride, calcium chloride, and ammonia are added to the solution of an alkali citrate, a precipitate will form in the cold only after many hours' standing or upon the addition of alcohol; but upon boiling the clear fluid, normal calcium citrate of the properties just stated will suddenly precipitate. By heating calcium citrate with ammonia and silver nitrate, the latter salt is not reduced, or only to a trifling extent.

4. *Lime-water* added in excess* produces no precipitate in cold solutions of citric acid or of citrates. But upon boiling some time with a tolerable excess of hot-prepared lime-water, a white precipitate of CALCIUM CITRATE is formed, the greater portion of which redissolves upon cooling.

5. *Barium acetate* added in excess to a solution of an alkali citrate, whether hot or cold, produces an amorphous precip-

* Alkali citrates dissolve calcium citrate, and are effective solvents for many compounds insoluble in water (barium sulphate, calcium phosphate, calcium oxalate, etc.). Hence sufficient calcium chloride or hydroxide must be added, so that the alkali citrate is fully decomposed by the reagent, in order that the reactions in 3 and 4, depending upon the separation of calcium citrate, may succeed.

itate of the formula $Ba_3(C_6H_5O_7)_2.7H_2O$. Barium hydroxide solution added in excess to citric acid produces the same precipitate. This does not make its appearance in dilute solutions, because it is not insoluble in water, but if such solutions are heated, a precipitate separates, which is first amorphous, and soon changes to microscopic needles of the formula $Ba_3(C_6H_5O_7)_2.5H_2O$. On heating this or the amorphous salt with excess of barium acetate for two hours on the water-bath, another very characteristic salt is formed. The latter consists of well-formed clinorhombic prisms, and has the formula $Ba_3(C_6H_5O_7)_2.3\frac{1}{2}H_2O$. If the solution is very dilute, the salt does not form till after evaporation. This is an infallible reaction for citric acid (H. KÄMMERER).

6. *Lead acetate* added in excess to a solution of citric acid produces a white, amorphous precipitate of LEAD CITRATE, which after washing is readily soluble in ammonia free from carbonate. By digestion for several hours with water or acetic acid on the water-bath, the precipitate becomes crystalline, and then has the formula $Pb_3(C_6H_5O_7)_2.3H_2O$. The microscope does not reveal the presence of well-formed crystals.

7. In solutions of normal citrates of the alkali metals, *silver nitrate* produces a white, flocculent precipitate of SILVER CITRATE, $Ag_3C_6H_5O_7$. On boiling a rather large quantity of this precipitate with only a little water, a gradual decomposition sets in, with separation of silver.

8. Upon heating citric acid or a citrate with *concentrated sulphuric acid* upon the water-bath, carbon monoxide escapes at first, then carbonic acid and acetone also, the sulphuric acid retaining its natural color. Upon continued boiling, however, the solution acquires a dark color, and sulphurous acid is evolved.

9. If citric acid (*e.g.*, .01 g) with excess of ammonia solution (3 cc) is introduced into a strong glass tube closed at one end, the tube is sealed in such a manner that only a small amount of free space is left above the liquid, and heated for six hours at 110° or 120°, and the liquid is then allowed to stand exposed to the air in a porcelain dish, an intensely blue or green product is obtained (difference from oxalic, tartaric, and malic acids, and means of detecting small amounts of citric acid in

the presence of these acids, SARANDINAKI, SABANIN and LASKOWSKY). This coloration characteristic for citric acid is also obtained when the acid is heated with a little thick glycerine (about .7 parts), at as low a temperature as possible, until the mass begins to puff up, the residue is dissolved in ammonia, the greater part of this is evaporated, and a little water and then two drops of red, fuming nitric acid which has been diluted with 5 parts of water, are added. Upon heating on the water-bath, the color, which is green at first, changes to blue (MANN). The reaction also appears when a minute amount of hydrogen peroxide is added instead of the nitric acid.

10. In relation to the microscopic detection of citric acid, see also HAUSHOFER, p. 75.

§ 199.

d. MALIC ACID, $H_2C_4H_4O_5$.

1. MALIC ACID crystallizes with difficulty, forming crystalline crusts or tufts of needles, which deliquesce in the air, and dissolve readily in water and in alcohol. The dilute aqueous solution of ordinary malic acid rotates a ray of polarized light towards the left (there is an artificial, inactive acid, and also one which is dextro-rotary). Exposed to a temperature of 140° or 150°, malic acid is slowly converted, with loss of water, into fumaric acid, $H_2C_4H_2O_4$. When heated between 150° and 200° in a glass tube or a retort, malic acid yields fumaric acid, which remains behind, while water and maleic anhydride, $C_4H_2O_3$, are given off. The latter then partially combines with water, forming maleic acid, $H_2C_4H_2O_4$. Upon heating above 200°, the fumaric acid also volatilizes, partly undecomposed. The crystalline sublimates produced, which are deposited in the glass tube above the heated part or in the neck of the retort, are very characteristic for malic acid. By heating with nitric acid, malic acid readily yields oxalic acid, with evolution of carbon dioxide.

2. With most bases, malic acid forms salts soluble in water Hydrogen potassium malate is not difficultly soluble in water; and therefore, potassium acetate fails to precipitate solutions of malic acid. This acid, like tartaric acid, prevents the precipitation of ferric hydroxide, etc., by alkalies.

3. If *calcium chloride*, ammonium chloride, and ammonia in excess are added to a solution of malic acid or an alkali-metal malate, the solution remains clear, and no precipitate is formed (if the amount of ammonium chloride was not too slight) even upon protracted boiling (difference from citric acid). If, however, two or three volumes of alcohol are added, CALCIUM MALATE, $CaC_4H_4O_5.3H_2O$, separates in white flocks. If the fluid is previously heated nearly to boiling, and hot alcohol is added in no greater quantity than is just necessary for the precipitation, the precipitate is deposited in the form of soft lumps, which adhere to the sides of the vessel; and on cooling, they harden and crumble by pressure to a crystalline powder (BARFOED). When heated with ammonia and silver nitrate, calcium malate causes no separation of silver, or hardly any. Calcium malate dissolves in boiling lime-water (difference and means of separation from calcium citrate, FLEISCHER).

4. *Lime-water* produces no precipitate in solutions of free malic acid, nor in solutions of malates. The fluid remains perfectly clear even upon boiling, provided the lime-water was prepared with boiling water.

5. *Lead acetate* throws down from solutions of malic acid and of malates, a white precipitate of LEAD MALATE, $PbC_4H_4O_5.3H_2O$. The precipitation is most complete if the fluid is neutralized by ammonia, as the precipitate is slightly soluble in free malic acid and acetic acid, and also in ammonia. If the liquid in which the precipitate is suspended is heated to boiling, a portion of the precipitate dissolves, and the remainder fuses to a mass resembling resin melted under water. Upon cooling the hot solution, the salt separates in needles or plates. To obtain this fusion of lead malate with small quantities, warm at first gently till the precipitate has shrunk together, then pour off the principal part of the fluid, and heat the rest with the precipitate to boiling. This reaction is distinctly marked only if the lead malate is

tolerably pure; for if mixed with other lead salts — or if, for instance, ammonia is added to alkaline reaction — it is only imperfect or fails altogether to make its appearance.

6. From solutions of normal malates of the alkali metals, *silver nitrate* throws down a white precipitate of SILVER MALATE, $Ag_2C_4H_4O_5$, which upon long standing or boiling turns a little gray.

7. On mixing the warm solution of free malic acid with *magnesia* or magnesium carbonate, till the acid reaction is destroyed, filtering, evaporating, and mixing the hot solution with hot alcohol, magnesium malate, $MgC_4H_4O_5$, separates as a glutinous mass on the sides of the vessel. It becomes hard upon cooling. Malic acid cannot be distinguished from citric acid by this reaction (BARFOED).

8. Upon heating malic acid with concentrated *sulphuric acid* on the water-bath, carbon dioxide and carbon monoxide are evolved at first; then the fluid turns brown and ultimately black, with evolution of sulphur dioxide.

9. In regard to the microscopic detection of malic acid, see HAUSHOFER, p. 67.

§ 200.

Recapitulation and Remarks.— Of the organic acids of this group, OXALIC ACID is characterized by the fact that gypsum solution causes a precipitation in solutions of the free acid, or of its alkali-metal salts acidified with acetic acid. TARTARIC ACID is characterized by the sparing solubility of the hydrogen potassium salt, the solubility of the calcium salt in cold solutions of sodium and potassium hydroxides, the reaction of the calcium salt with ammonia and silver nitrate, and the peculiar odor which the acid and its salts emit upon heating. It is most safely detected in presence of the other acids by means of potassium acetate or potassium fluoride (§ 197, 4). Without considering the reactions which are based upon the observation of characteristic tartaric acid salts, the reactions given in § 197,

11, 13, 14, and 15, allow tartaric acid to be distinguished from citric, malic, and also succinic acids, and permit its detection in their presence. Reaction 12 is also well adapted for the detection of tartaric acid in the presence of citric acid, for the latter gives only a lemon-yellow and no brownish to reddish liquid when heated in a test-tube upon the water-bath with concentrated sulphuric acid (1 g with 10 cc). (E. SCHMIDT, PUSCH).* CITRIC ACID is usually recognized by its reaction with lime-water, or with calcium chloride and ammonia in presence of ammonium chloride; but in this, the absence or the removal of oxalic and tartaric acids is always presupposed, and also the employment of a sufficient quantity of lime-water or a properly regulated amount of calcium chloride. A very safe characteristic of citric acid consists in the microscopic appearance of its barium salt (§ 198, 5), and also the production of the blue or green decomposition product mentioned in § 198, 9. MALIC ACID would be sufficiently characterized by the deportment of lead malate when heated under water, were this reaction more sensitive, and not so easily prevented by the presence of other acids. The safest means of identifying malic acid is to convert it into maleic acid and fumaric acid by heating in a glass tube; but this conversion can be effected successfully only with pure malic acid. Lead malate is sparingly soluble in ammonia, while the citrate and tartrate of lead dissolve freely in ammonia which is free from carbonic acid. This different deportment of the lead salts of the acids affords a means of distinguishing them. Calcium citrate and malate may be separated by means of boiling lime-water, which dissolves the latter and leaves the former behind. Malic acid may be detected also in the presence of citric (and succinic) acid by mixing the solution, after acidifying it with a few drops of sulphuric acid, with a little potassium dichromate, and heating to boiling, whereupon, in the presence of malic acid, an odor of fresh apples is given off (PAPASOGLI and POLI). If only one of the four acids is present in a solution, lime-water will suf-

* Concerning the distinction of tartaric acid from the other organic acids by means of hexamine cobaltic chloride, compare C. D. BRAUN, Zeitschr. f. analyt. Chem., 7, 349.

fice to indicate which one it is; since malic acid is not precipitated by this reagent, citric acid is precipitated only upon boiling, while tartaric acid and oxalic acid are thrown down in the cold, and the calcium tartrate redissolves upon addition of ammonium chloride, while the oxalate does not. If the four acids together are present in a solution, the oxalic and tartaric acids are usually precipitated first by calcium chloride and ammonia, in presence of ammonium chloride. But it must be noted here that the calcium tartrate requires some time (about two hours) for a precipitation that is tolerably complete (it is separated from the oxalate by sodium hydroxide solution), and also that an alkali citrate when present in any quantity prevents the thorough separation of oxalic acid and still more of tartaric acid. On cautiously adding alcohol in moderate quantity to the filtrate, the calcium citrate separates (and with it the rest of the calcium oxalate and tartrate). On filtering, and mixing the filtrate with more alcohol, calcium malate is thrown down. From the latter, the acid is prepared by dissolving it in acetic acid, adding alcohol, filtering if necessary, mixing the filtrate with lead acetate, neutralizing with ammonia, washing the precipitate, suspending it in water, treating with hydrogen sulphide, filtering, and evaporating the filtrate to dryness.

A better method for the detection of malic acid in the presence of the three other acids consists in combining the acids with ammonia, concentrating strongly, neutralizing the still warm fluid with ammonia (to dissolve the acid salts produced during the evaporation), and adding 8 volumes of alcohol of 98 per cent. After 12 or 24 hours, the solution of ammonium malate is filtered from the undissolved oxalate, tartrate, and citrate of ammonium, the malic acid is precipitated with lead acetate, and the acid prepared from the precipitate is tested further (BARFOED). Where a small quantity of citric or malic acid is to be detected in presence of a large proportion of tartaric acid, the best way is to first remove the latter by potassium acetate, with addition of an equal volume of strong alcohol. The other acids may then be completely precipitated in the filtrate by excess of calcium chloride and ammonia, if the quantity of the alcohol is a little increased. The calcium malate may be finally

separated from calcium citrate by treatment with boiling hot lime-water.*

§ 201.

Racemic Acid, $H_2C_4H_4O_6$.

The formula of crystallized RACEMIC ACID is $C_4H_6O_6.H_2O$. The water of crystallization escapes slowly in the air, but rapidly at 100° (difference between racemic acid and tartaric acid). To solvents, racemic acid comports itself like tartaric acid. The RACEMATES also show very similar deportment to that of the tartrates. However, many of them differ from the corresponding tartrates in the amount of water they contain, and in form and solubility. The aqueous solution of racemic acid and the racemates exercises no diverting action upon polarized light (difference from dextro- and lævo-tartaric acids). From the solutions of free racemic acid and of racemates, *calcium chloride* precipitates CALCIUM RACEMATE, $CaC_4H_4O_6.4H_2O$, as a white, crystalline powder. Ammonia throws down the precipitate from its solution in hydrochloric acid, either immediately or at least very speedily (difference from tartaric acid). It dissolves in solution of sodium or potassium hydroxide, but is reprecipitated from this solution by boiling (difference from oxalic acid). *Lime-water* added in excess immediately produces a white precipitate insoluble in ammonium chloride and also in acetic acid (difference from tartaric acid). Solution of *calcium sulphate* does not immediately produce a precipitate in a solution of racemic acid (difference from oxalic acid); but after ten or fifteen minutes, calcium racemate separates (difference from tartaric acid), and in solutions of normal racemates, the precipitate forms immediately. With *potassium salts*, racemic acid comports itself like tartaric acid. By letting sodium potassium racemate or sodium ammonium racemate crystallize, two kinds of crystals are obtained, which resemble each other as the image reflected by a mirror resembles the object reflected. One kind of crystals contains common or dextro-tartaric acid (which turns the plane of polarized light towards the right); the other kind contains lævo-tartaric acid, *i.e.*, an acid which is the same in every respect as tartaric acid, with this exception only, that it turns the polarized light towards the left. If the two kinds of crystals are redissolved together, the solution shows again the reactions of the racemic acid. In regard to the microscopic detection of this acid, see HAUSHOFER, p. 32.

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* Concerning the separation of malic acid from citric, as well as succinic acid, see also MICKO. Zeitschr. f. analyt. Chem. 31. 465; and concerning the separation of malic, citric, and succinic acids, see also W. KEIM, *ibid.*, 30. 405.

Second Group of Organic Acids.

The acids of the second group sublime without alteration, or are decomposed only to the anhydride and water. By heating with nitric acid, they are either left unchanged (succinic acid), or merely converted into nitro-acids (benzoic acid, salicylic acid). The calcium salts are readily soluble in water (benzoic acid, salicylic acid), or are difficultly soluble (succinic acid). The solutions of the normal alkali-metal salts are precipitated (succinic and benzoic acids) or very intensely colored (salicylic acid) by ferric chloride: SUCCINIC ACID, BENZOIC ACID, SALICYLIC ACID.

§ 202.

a. Succinic Acid, $H_2C_4H_4O_4$.

1. Succinic acid forms colorless and inodorous prisms or tables. It is readily soluble in hot water and hot alcohol, more difficultly soluble in the cold liquids, and slightly soluble in ether (1.265 : 100). When heated for a considerable time to 140°, the acid sublimes, partly undecomposed, and partly yielding water and the sublimed anhydride. When rapidly heated, the acid fuses at 180° and boils at 235°, whereupon it is mostly decomposed into water and the anhydride. The sublimed anhydride forms needles with a silky luster. When heated in the air, succinic acid burns with a blue flame free from soot. When pure, the acid is odorless and has a slight, acid taste. The officinal acid, which has an empyreumatic odor, leaves a moderate carbonaceous residue upon volatilization. Succinic acid is not destroyed by heating with nitric acid, and may therefore be easily obtained in the pure state by boiling with that acid for half an hour, by which means any oil of amber present is destroyed.

2. The succinates are decomposed at a red heat; and those which contain alkali or alkali-earth metals are converted into carbonates, with separation of charcoal. Many

of the succinates are soluble in water. Sodium succinate is scarcely soluble in strong alcohol, and crystallizes well both as normal and acid salt; hence it may be readily obtained in a pure state from very impure fluids. This property may be utilized for the detection and separation of the acid.* On heating the succinates with potassium disulphate in a tube, the acid sublimes. It may be also obtained from the salts by decomposing them with sulphuric acid, and extracting with warm absolute alcohol, and also by repeatedly shaking the solution, strongly acidified with sulphuric acid, with ether, when almost all the succinic acid is obtained in the ethereal solution.

3. If *calcium chloride*, ammonium chloride, and ammonia in excess are added to a solution of succinic acid or of an alkali-metal succinate, the liquid remains clear in the cold, and also upon boiling if the amount of ammonium chloride was not too small. But if two or three volumes of alcohol are added, CALCIUM SUCCINATE, $CaC_4H_4O_4.3H_2O$, separates (often only after some time) in a crystalline condition.

4. *Barium chloride* produces in solutions of alkali succinates, but not in solutions of free succinic acid, usually only after some time, a white, crystalline precipitate of BARIUM SUCCINATE, $BaC_4H_4O_4$. Warming facilitates the separation, and upon the addition of alcohol, it separates quickly, even from dilute solutions.

5. In a solution of a normal alkali succinate, *ferric chloride*, carefully treated with very dilute ammonia until the solution has a dark, brownish-red color, but is still clear, produces a pale brownish-red, voluminous precipitate of BASIC FERRIC SUCCINATE, $2Fe_2(C_4H_4O_4)_3.Fe_2O_3$. The precipitate dissolves readily in mineral acids, but difficultly in cold acetic acid. It is decomposed by ammonia, which causes the separation of a highly basic ferric succinate of a less bulky nature, while the greater part of the succinic acid goes into solution as ammonium succinate. Alkali tartrates prevent or interfere with the precipitation of the basic ferric succinate.

6. *Lead acetate*, when added drop by drop to a solution of free succinic acid, or of an alkali succinate, produces a white

* Compare MEISSNER and JOLLY, Zeitschr. f. analyt. Chem., 4, 502.

amorphous precipitate, which is immediately redissolved in excess of succinic acid, in alkali succinate, and in lead acetate, but in a short time separates from such solutions in the crystalline form. The latter precipitate consists of normal LEAD SUCCINATE, $PbC_4H_4O_4$, which is barely soluble in water, even when boiling, as well as in succinic acid and lead acetate, readily soluble in nitric acid, and dissolves somewhat more difficultly in acetic acid. By ammonia it is converted into a basic salt.

7. In regard to the microscopic detection of succinic acid, see HAUSHOFER, p. 73.

§ 203.

b. BENZOIC ACID, $HC_7H_5O_2$.

1. BENZOIC ACID forms white scales or needles, or simply a crystalline powder. It is odorless in the pure state, but usually has a faint aromatic odor. It fuses at 121.4°, and boils at 250°, volatilizing completely. When heated in an open dish, it evaporates in considerable quantity even at 100°. The fumes cause a peculiar, irritating sensation in the throat, and provoke coughing; when cautiously cooled, they condense to brilliant needles; and when kindled, they burn with a luminous, sooty flame. The common officinal benzoic acid has the odor of benzoin, and leaves a small, carbonaceous residue upon volatilization. Benzoic acid dissolves at 0° in 588, at 20° in 345, and at 100° in 17 parts of water (BOURGOIN). It is taken up readily by alcohol as well as by ether. Addition of water imparts, therefore, a milky turbidity to a saturated solution of the acid in alcohol. The solutions of benzoic acid have an acid reaction. The acid dissolves in concentrated sulphuric acid to a colorless liquid, from which it is separated by water unchanged.

2. Most of the BENZOATES are soluble in water, only those with weak bases (*e.g.*, ferric benzoate) being insoluble. The soluble benzoates have a peculiar, pungent taste. The addition of a *strong acid* to CONCENTRATED aqueous solutions of benzoates displaces the benzoic acid, which separates in the form of a dazzling white, sparingly soluble, crystalline powder.

In the same way, benzoic acid is separated from the insoluble benzoates by such strong acids as form soluble salts with the bases with which the benzoic acid is combined.

3. *Ferric chloride*, carefully mixed with very dilute ammonia until the solution has a dark brownish-red color, but is still clear, precipitates all the benzoic acid in combination with ferric oxide, from solutions of normal alkali benzoates. The voluminous, flesh-colored precipitate, BASIC FERRIC BENZOATE, $Fe_2(C_7H_5O_2)_6.Fe_2O_3.15H_2O$, is decomposed (similarly to basic ferric succinate) by treatment with ammonia, but it is distinguished from the succinate by the fact that it dissolves in a little hydrochloric acid, with the separation of the greater part of the benzoic acid. Alkali tartrates prevent or interfere with the precipitation of basic ferric benzoate.

4. *Lead acetate* fails to precipitate free benzoic acid, but it produces flocculent precipitates in solutions of alkali benzoates. The precipitate, $Pb(C_7H_5O_2)_2.H_2O$, is insoluble in sodium benzoate, but dissolves in an excess of the lead acetate, and also in acetic acid. Upon heating to boiling the solution in which the precipitation has taken place, the precipitate does not dissolve, nor does it dissolve in ammonia.

5. A mixture of *alcohol*, *ammonia*, and *barium* or *calcium chloride*, produces no precipitate in solutions of benzoic acid or of the alkali benzoates (difference from succinic acid).

6. In relation to the microscopic detection of benzoic acid, see HAUSHOFER, p. 71.

§ 204.

c. SALICYLIC ACID, $HC_7H_5O_3$.

1. SALICYLIC ACID crystallizes in colorless, odorless prisms. It dissolves only slightly in cold water, but more readily in hot water; 1 part requires for solution 666 parts of water at 0°, 370 parts at 20°, and 12.6 parts at 100° (BOURGOIN). It dissolves very abundantly in alcohol and in ether, and also in amyl alcohol and chloroform. It fuses at 155°, and with careful heating sublimes unchanged in needles. When heated quickly and strongly, it is partly decomposed into carbonic

acid and phenol. When an aqueous solution of salicylic acid is boiled, the acid volatilizes in considerable quantity. The aqueous solution gives a distinctly acid reaction. By the action of strong nitric acid upon salicylic acid, with the aid of heat, nitro-salicylic acids are produced.

2. Salicylic acid forms TWO SERIES OF SALTS with bases, which are usually designated as NORMAL and BASIC SALTS. The solutions of the alkali salts, especially when containing basic salts, become colored brownish by heating in the air. Most of the normal salicylates are easily soluble in water, but many of the basic salts are insoluble or slightly soluble in that liquid. Most of the salicylates give off phenol upon being heated. From sufficiently concentrated solutions, *mineral acids* precipitate salicylic acid as a white, crystalline precipitate. Acetic acid produces no precipitation.

3. If a small amount of a very dilute *ferric chloride* solution is added to an aqueous solution of salicylic acid or one of its salts, the liquid becomes colored intensely violet. Free acetic acid, lactic acid, and butyric acid interfere with the delicacy of this very characteristic reaction. Hydrochloric acid as well as ammonia destroy it.

4. In solutions of normal alkali salicylates, *lead acetate* produces a white precipitate of lead salicylate, $Pb(C_7H_5O_3)_2.H_2O$, which is soluble in an excess of lead acetate and also in acetic acid, but not in ammonia. When the precipitate is heated with the liquid from which it was formed, it dissolves, and separates in crystals upon cooling.

5. Neither *calcium chloride* nor *barium chloride* precipitates solutions of alkali salicylates, not even upon the addition of ammonia and alcohol.

6. If a solution of salicylic acid in *methyl alcohol* is mixed with half its volume of concentrated sulphuric acid, and heated, METHYL SALICYLATE is formed, a compound with an aromatic odor, which is the chief constituent of oil of wintergreen. This may be collected by distillation. With a solution of salicylic acid in ordinary alcohol, the analogous ethyl compound with a similar odor is obtained.

§ 205.

Recapitulation and Remarks.—Benzoic and salicylic acids are especially distinguished from succinic acid, by the fact that the latter is far more soluble in water than the others, from which it follows that benzoic and salicylic acids are precipitated from the concentrated solutions of their salts by mineral acids.

Succinic and benzoic acids are distinguished from salicylic acid by the fact that they are precipitated by ferric chloride, while the latter is not precipitated, but causes an intense violet coloration of the liquid. If the basic ferric salts which separate are decomposed by digestion with ammonia, the liquid is filtered, and the filtrate is concentrated, the benzoic acid may be separated by the addition of acid, and the succinic acid may be detected as barium or calcium succinate. Succinic acid may be also separated from salicylic acid by precipitation as the calcium or barium salt.

If it is desired to separate the three acids or one of them from a liquid containing other organic substances, this may be accomplished by repeatedly extracting the liquid with ether after acidifying it strongly with sulphuric acid. If the ether is distilled off, the acids remain behind. In connection with the detection of salicylic acid in wine, in order to prevent tannic acid from also going into the solution, it is better to shake the acidified wine (about 50 cc) with a mixture of equal parts of ether and petroleum-ether, to evaporate the separated layer of the solvent, after the addition of a little water, upon the water-bath, and to test the residue with ferric chloride (§ 204, 3). Instead of the mixture of ether and petroleum-ether, carbon disulphide or amyl alcohol may be used.

Succinic, benzoic, and salicylic acids do not prevent the precipitation of ferric oxide, alumina, etc., by the alkalies.*

* In relation to a method for the separation of salicylic acid from benzoic acid, see also, J. SCHAAP, Zeitschr. f. analyt. Chem., 32, 107.

Third Group of Organic Acids.

The acids of the third group may be distilled with water (lactic acid with difficulty). The calcium salts are readily soluble in water. The solutions of the normal alkali-metal salts are not precipitated in the cold by ferric chloride: ACETIC ACID, FORMIC ACID (*lactic acid, propionic acid, butyric acid*).

§ 206.

a. ACETIC ACID, $HC_2H_3O_2$.

1. ACETIC ACID forms transparent, crystalline scales, which fuse at 17° to a colorless fluid of a peculiar, pungent, and penetrating odor and exceedingly acid taste. It boils at 119°, and volatilizes completely, forming pungent vapors, which burn with a blue flame. It is miscible with water in all proportions. It is to such mixtures of the acid with water that the name of acetic acid is commonly applied. Acetic acid is also soluble in alcohol.

2. The ACETATES undergo decomposition at a red heat. When thus ignited, the alkali salts and other salts with strong bases yield chiefly acetone, C_3H_6O, and carbon dioxide, the latter, according to the nature of the base, either remaining combined with the base or escaping. The acetates with weak bases allow a large part of the acetic acid to escape unchanged. The residues left upon igniting acetates are usually carbonaceous. Nearly all acetates dissolve in water and in alcohol; most of them are readily soluble in water, while a few only are difficult of solution in that liquid. If acetates are distilled with dilute sulphuric acid, free acetic acid is obtained in the distillate.

3. If *ferric chloride* is added to acetic acid, and the acid is then nearly saturated with ammonia, or if a neutral acetate is mixed with ferric chloride, the fluid acquires a deep red color, owing to the formation of FERRIC ACETATE. By boiling, the fluid becomes colorless if it contains an excess of acetate, the

whole of the iron precipitating as a basic acetate, in the form of brownish-yellow flocks. Ammonia precipitates from the solution of ferric acetate the whole of the iron as hydroxide. By addition of hydrochloric acid, a fluid which appears red from the presence of ferric acetate turns yellow (difference from ferric sulphocyanide).

4. Neutral acetates (but not free acetic acid, if somewhat diluted) give with *silver nitrate* white, crystalline precipitates of SILVER ACETATE, $AgC_2H_3O_2$, which are very sparingly soluble in cold water. They dissolve more easily in hot water, but upon cooling, separate again in the form of very small crystals. Ammonia dissolves them readily, but free acetic acid does not increase their solubility in water.

5. *Mercurous nitrate* produces with acetic acid, and more readily still with acetates, white, scaly, crystalline precipitates of MERCUROUS ACETATE, $Hg_2(C_2H_3O_2)_2$, which are sparingly soluble in water and acetic acid in the cold, but dissolve without difficulty in an excess of the precipitant. The precipitates dissolve in water upon heating, but separate again in the form of small crystals upon cooling. In this process, the salt undergoes partial decomposition, and a portion of the mercury separates in the metallic state, imparting a gray color to the precipitate. If the mercurous acetate is boiled with dilute acetic acid instead of water, the quantity of the metallic mercury which separates is exceedingly minute.

6. *Mercuric chloride* produces no precipitate of mercurous chloride with acetic acid or acetates upon heating.

7. By heating acetates with *concentrated sulphuric acid*, ACETIC ACID is evolved, which may be known by its pungent odor. But if the acetates are heated with a mixture of about equal volumes of *concentrated sulphuric acid* and *alcohol*, ETHYL ACETATE, $(C_2H_5)C_2H_3O_2$, is formed. The odor of this ether is highly characteristic and agreeable. It is most distinct upon shaking the mixture when somewhat cooled, and is much less liable to lead to mistakes than the pungent odor of the acid.

8. If dilute acetic acid is heated with an excess of *lead oxide*, part of the latter dissolves as basic lead acetate. The fluid has an alkaline reaction, and gives no crystals on cooling.

9. In regard to the microscopic detection of acetic acid, see HAUSHOFER, p. 76.

§ 207.

b. Formic Acid, $HCHO_2$.

1. Formic acid is a transparent and colorless, corrosive, slightly fuming liquid, with a characteristic and exceedingly penetrating odor. It crystallizes at $-1°$ in colorless plates. It is miscible in all proportions with water and alcohol. It boils at 98.5°, and distils without decomposition. The vapors burn with a blue flame.

2. Upon ignition, the formates, like the corresponding acetates, leave behind either carbonates, oxides, or metals, the process being attended with the separation of charcoal, and the escape of combustible gases, carbon dioxide, and water. All the compounds of formic acid with bases are soluble in water, and alcohol also dissolves many of them, but not all.

3. Formic acid shows the same reaction as acetic acid with *ferric chloride.*

4. *Silver nitrate* fails to precipitate free formic acid, and gives a precipitate with the alkali formates in concentrated solutions only. The white, sparingly soluble, crystalline precipitate of silver formate, $AgCHO_2$, acquires a darker tint very rapidly, owing to the separation of metallic silver. Complete reduction of the silver to the metallic state takes place after the lapse of some time, even in the cold; but immediately upon applying heat to the fluid containing the precipitate. The same separation of metallic silver occurs in a solution of free formic acid, and also in solutions of formates so dilute that the addition of the silver nitrate fails to produce a precipitate, but it does not take place in presence of an excess of ammonia. In this reaction, formic acid removes oxygen from the silver oxide; carbonic acid, which escapes, and water are formed, and the metal separates.

5. *Mercurous nitrate* gives no precipitate with free formic acid; but in solutions of alkali formates, this reagent produces a glistening white, sparingly soluble precipitate of mercurous formate, $Hg_2(CHO_2)_2$, which rapidly becomes gray, owing to the separation of metallic mercury. Complete reduction ensues, even in the cold, after the lapse of some time, but is immediate upon application of heat. This reduction

is also attended with the formation of carbon dioxide and water, and takes place both in fluids so highly dilute that the mercurous formate is retained in solution and in solutions of free formic acid.

6. If formic acid or an alkali formate is heated with *mercuric chloride*, MERCUROUS CHLORIDE precipitates before the liquid has reached the boiling-point. Presence of free hydrochloric acid or of rather large quantities of alkali-metal chlorides prevent the reaction.

7. If formic acid or a formate is heated with *concentrated sulphuric acid*, the formic acid is resolved, without blackening, into water and CARBON MONOXIDE gas. The latter escapes with effervescence, and, if kindled, burns with a blue flame. The sulphuric acid removes from the formic acid the water necessary for its existence, and thus causes a transposition of its elements: $CH_2O_2 = H_2O + CO$. Upon heating formates with dilute sulphuric acid in a distilling apparatus, free formic acid is obtained in the distillate, and may usually be readily detected by its odor. Upon heating a formate with a mixture of strong sulphuric acid and alcohol, ETHYL FORMATE is evolved, which is characterized by its peculiar rum-like smell.

8. If dilute formic acid is heated with excess of *lead oxide*, the latter partially dissolves. The fluid has an alkaline reaction, and on cooling the solution, which is concentrated by evaporation if necessary, LEAD FORMATE, $Pb(CHO_2)_2$, separates in brilliant prisms or needles.

9. Concerning the microscopic detection of formic acid, see HAUSHOFER, p. 68.

§ 208.

Recapitulation and Remarks.—Acetic and formic acids are readily distinguished from the other organic acids by the fact that they can be distilled with water, and form with ferric oxide, soluble normal salts which dissolve in water with a blood-red color, and are decomposed by boiling. The two acids are distinguished from each other by their odor and that of their ethyl compounds, and by their different reactions with silver salts and salts of mercury, with lead

oxide, and with concentrated sulphuric acid. The separation of acetic from formic acid is effected by heating the mixture of the two acids with an excess of mercuric or silver oxide. Formic acid reduces the oxide and suffers decomposition, while the acetic acid dissolves the oxide and remains in solution as an acetate. The separation may be also effected by boiling the free acids for ten minutes with an equal volume of a solution of potassium dichromate and sulphuric acid* in connection with an inverted condenser, by which means the formic acid is oxidized to water and carbonic acid, while the acetic acid remains unchanged, and may be obtained from the residue by distillation (MACNAIR).

§ 209.

Rarer Organic Acids of the Third Group.

1. LACTIC ACID, $HC_3H_5O_3$.

LACTIC ACID occurs in animal fluids, vegetable matters that have turned sour, etc. When as pure as possible, it is a colorless, syrupy liquid, which is odorless and has a pure, sharp, acid taste. When it is slowly heated in a retort to 130°, water containing a little lactic acid distils over, leaving a residue of lactic anhydride, which between 250° and 300° is decomposed into carbon monoxide, carbon dioxide, lactide, and other products. Lactic acid dissolves freely in water, alcohol, and ether. Upon boiling the aqueous solution, a little lactic acid volatilizes with the aqueous vapor. If a little lactic acid is added to a solution of *phenol made blue with ferric chloride*, the blue color changes to yellow. The reaction is delicate (UFFELMANN), but it should be noticed that butyric acid behaves in a similar manner. All the lactates are soluble in water, the greater part of them, however, only sparingly. They behave similarly with alcohol. *Lead acetate* with the addition of *alcoholic ammonia* produces a granular-sandy precipitate, which is insoluble in alcohol (PALM). The lactates are insoluble in ether. The production of some of the salts and the examination of their form under the microscope supply the means for the detection of lactic acid; and calcium and zinc lactates are the best suited for this purpose. Calcium lactate may be conveniently prepared from animal or vegetable juices by the following method devised by SCHERER: Dilute the liquid, if necessary, with water, mix with baryta-water, and filter. Distil the filtrate with some sulphuric acid (to remove volatile acids), digest the residue several days with strong alcohol,

* 12 g potassium dichromate, 100 cc water, and 30 cc concentrated sulphuric acid.

distil the acid solution with a little milk of lime, filter, while warm, from the excess of lime and calcium sulphate, conduct carbon dioxide into the filtrate, heat once more to boiling, filter from the precipitated calcium carbonate, evaporate the filtrate, warm the residue with strong alcohol, filter, and let the neutral filtrate stand several days to give the calcium lactate time to crystallize. Should the quantity of lactic acid present be insufficient to allow the formation of crystals, evaporate the fluid to syrupy consistence, mix with strong alcohol, let the mixture stand some time, decant or filter the alcoholic solution into a vessel that can be closed, and add gradually small quantities of ether. This process will cause even traces of calcium lactate to separate from the fluid. For the preparation from urine of a lactic acid which is adapted for obtaining the characteristic salts, SCHULTZEN and RIESS recommend the following method: Concentrate the urine very much, precipitate warm with 95 per cent alcohol, and pour off the alcoholic solution after twenty-four hours, evaporate it to a syrup, acidify with dilute sulphuric acid, and extract by shaking with ether. Distil the ethereal solution, dissolve the residue in water, precipitate with basic lead acetate, filter, treat the filtrate with hydrogen sulphide, filter again, and drive off the acetic acid by repeated evaporation upon the water-bath. Under the microscope, calcium lactate appears in the form of tufts of needles. Two of the tufts are always joined together by their short stems, so that they are like two united brushes. Zinc lactate, after rapid separation, appears under the microscope in the form of spherical groups of needles. Slow evaporation of the zinc lactate solution gives at first crytals resembling clubs truncated at both ends. These crystals gradually grow, the two ends apparently diminishing, while the middle parts predominate (FUNKE).

§ 210.

2. PROPIONIC ACID, $HC_3H_5O_2$; and 3. BUTYRIC ACID, $HC_4H_7O_2$.

PROPIONIC ACID is formed under a great variety of circumstances, and is chiefly found in fermented liquids. The pure acid is a colorless liquid, having a very acid odor and taste, which boils at 140.5° and does not solidify even at −21°. It dissolves readily in water, and floats as an oily stratum on concentrated aqueous solution of phosphoric acid and on solution of calcium chloride. It has a peculiar smell, which reminds one of both butyric and acetic acids. Upon distilling the aqueous solution, the propionic acid passes over into the distillate. BUTYRIC ACID is frequently found in animal and vegetable matter, more particularly in fermented liquids of various kinds. The pure acid is a colorless, mobile, corrosive, intensely sour fluid boiling at 163°, of a disagreeable odor, a combination of the smell of rancid butter and acetic acid. It is miscible in all proportions with water and alcohol. It is separated from the concentrated aqueous solution by calcium chloride, concentrated acids, etc., in the form of a thin

oil. The smell of butyric acid is particularly strong in the aqueous solution of the acid. Upon distilling the aqueous solution, the acid passes over with the aqueous vapors.

Propionic acid and butyric acid are often found associated with each other, and with formic and acetic acids, in fermented liquids, guano, urine, and many mineral waters. In such cases, the detection of the several acids may be effected as follows: Dilute the substance sufficiently with water, acidify with sulphuric acid, and distil. Saturate the distillate with baryta-water, evaporate to dryness, and treat the residue repeatedly with boiling alcohol of 85 per cent. This will leave the barium formate and part of the barium acetate, the remainder of the acetate, together with the propionate and butyrate, dissolving in the alcohol. Evaporate the alcoholic solution, dissolve the residue in water, decompose cautiously with silver sulphate, boil, filter, and let the fluid (which ought to contain a little undecomposed barium salt rather than any silver sulphate) evaporate under the desiccator. Take out separately the crystals which form first, those which form later, and those which form last, and examine them to ascertain their nature. Upon solution in concentrated sulphuric acid, silver acetate emits the odor of acetic acid, and gives no oily drops; but silver propionate and butyrate emit the peculiar odor of the acids, and give oily drops, which with minute quantities, however, are visible only under the microscope. To distinguish positively between propionic and butyric acid, it is indispensable to determine the amount of silver in the separated silver salts, and thus fix the molecular weight of the acids. If much barium acetate has passed into the solution, with a small quantity only of butyrate and propionate, the barium is first exactly precipitated with sulphuric acid (in the aqueous solution of the barium salts soluble in alcohol), one half of the acid fluid neutralized with caustic soda, the other half added, the fluid then distilled, the distillate (which now contains principally propionic and butyric acids) neutralized with baryta, then decomposed with silver sulphate, and the remaining part of the process conducted as above.

The following process may be also used with advantage for the separation of propionic acid from acetic and formic acids: Evaporate the mixture of the three acids with water and an excess of lead oxide to dryness, triturate the residue with the addition of lukewarm water, allow this to stand for twelve hours at the temperature of the room, and filter. Besides some of the lead formate and acetate, the filtrate contains all the propionic acid as a basic lead salt. If the solution is now boiled, the latter separates, and if filtered hot, it is obtained upon the filter, while the part of the lead acetate and formate which had gone with it into solution are obtained in the filtrate (LINNEMANN). Butyric acid, and also acetic acid, may be separated from formic acid by the behavior of the acids with mercuric chloride upon boiling, for under these circumstances, the formic acid only is decomposed (§ 207, 6, SCALA).

PART II.

SYSTEMATIC COURSE

OF

QUALITATIVE CHEMICAL ANALYSIS.

PRELIMINARY REMARKS.

THE knowledge of reagents and of the deportment of bodies with them enables us to ascertain at once whether a compound, of which the physical properties permit an inference as to its nature, is in reality what we suspect it to be. For instance, a few simple reactions suffice to show that a body which appears to be calcite is really calcium carbonate, and that another which is held to be gypsum is actually calcium sulphate. This knowledge usually suffices, also, to ascertain whether a certain body is present or not in a mixture; for instance, whether or not a white powder contains mercurous chloride. But if our design is to ascertain the chemical nature of a substance entirely unknown to us—if we wish to discover *all* the constituents of a mixture or chemical compound—if we intend to prove that, besides certain bodies which we have detected, no other substance *can* possibly be present—if, consequently, a *complete* qualitative analysis is our object, the mere knowledge of the reagents, and of the reactions of bodies with them, will not suffice for the attainment of this end. This requires the additional knowledge of a *systematic course* of analysis; in other words, the knowledge of

the *order* in which solvents, and general and special reagents, should be applied, both to effect the speedy and certain detection of every element present, and to prove with certainty the absence of all others. If we do not possess the knowledge of this systematic course, or if, in the hope of attaining our object more rapidly, we adhere to no method, analyzing becomes (at least in the hands of a novice) mere guesswork, and the results obtained are no longer the fruits of scientific calculation, but mere matters of accident, which occasionally may prove lucky hits, and at other times total failures.

Every analytical investigation must therefore be based upon a definite method, but it is not by any means necessary that this method should be the same in all cases. Practice, reflection, and a due attention to circumstances will, on the contrary, generally lead to the adoption of different methods for different conditions. However, all analytical methods agree in this, that the substances to be looked for are in the first place classed into groups, which are then subdivided, until the individual detection of the various substances present is finally accomplished. The diversity of analytical methods depends partly on the order in which reagents are applied, and partly upon their selection.

Before we can venture upon inventing methods of our own for individual cases, we must first make ourselves thoroughly conversant with a course of chemical analysis in general. This system must have passed through the ordeal of experience, and must be adapted to every imaginable case, so that afterwards, when we have acquired some practice in analysis, we may be able to determine which modification of the general method will be best adapted to a given case.

The exposition of such a systematic course, adapted to all cases, tested by experience, and combining simplicity with the greatest possible security, is the object of the *First Section*.

The elements and compounds comprised in it are the same that we have studied in Part I., with the exception of those discussed more briefly, and marked by the use of smaller type.

The method of presentation is one which leads directly to practical investigation, so that all careful observers will attain the desired result with speed and certainty, and cannot go astray in following the course.

The subdivisions of this systematic course are—1. Preliminary examination; 2. Solution; 3. Actual Analysis.

Actual analysis, however, is again divided into the investigation of compounds in which it is assumed that only *one* base and *one* acid are present, and the analysis of mixtures or compounds in which *all* the bodies here taken into consideration are assumed to be present. With respect to the latter, it should be remarked that where the preliminary examination has not clearly demonstrated the absence of certain groups of substances, the student cannot safely disregard any of the paragraphs to which reference is made, in consequence of the reactions he has observed. In cases where the intention is simply to test a mixture for certain substances, and not to ascertain all its constituents, it will be easy to select the particular paragraphs to which attention should be given.

As the construction of a universally applicable systematic course of analysis requires due provision for every contingency that may possibly arise, it is self-evident that, though in the system here laid down the various bodies comprised in it have been assumed to be mixed up together in every conceivable way, it was absolutely indispensable to assume that no foreign *organic matters* were present, since the presence of such matters would conceal many reactions, and introduce various complications into others.

Although the general analytical course laid down here is devised and arranged in a manner to suit all possible contingencies, still there are special cases in which it may be advisable to modify it. A preparatory treatment of the substance is also sometimes necessary before the actual analysis can be proceeded with, and the presence of coloring or slimy organic matters more especially requires certain preliminary operations. The *Second Section* will be found to contain a detailed description of the special methods employed to meet certain cases which frequently occur. Some of these methods show how the analytical process becomes simplified as the number of substances to be considered decreases.

In conclusion, as an intelligent and successful pursuit of analysis is possible only with an accurate knowledge of the principles whereon the detection and separation of bodies depend, I have given in the *Third Section* an explanation of

the general analytical process, with numerous additions to the practical operations. As this third section may properly be regarded as the key to the first and second, students are strongly recommend to make themselves thoroughly acquainted with it at the outset. A special section is devoted to this theoretical explanation, as I think it will be understood better in a connected form than it would have been by explanatory additions to the several paragraphs, which, moreover, might have materially interfered with the perspicuity of the practical process.

In this third section, I have also taken occasion to point out in what residues, solutions, precipitates, etc., which are obtained in the systematic course of analysis, the *rarer elements*, *acids*, or *radicals* may be expected to be met with; and also to give instructions how to proceed systematically, with a view to insure the detection of these bodies.

SECTION I.

PRACTICAL PROCESS FOR THE ANALYSIS OF COMPOUNDS AND MIXTURES IN GENERAL.

I. Preliminary Examination.*

Examine, in the first place, the external properties of 1† the substance, such as the color, shape, hardness, gravity, odor, etc., since these will often enable one in some measure to infer its nature. Before proceeding, if the quantity of the substance is limited, the operator must consider how much may safely be spared for the preliminary examination. A reasonable economy is in all cases advisable, for the sake of cultivating the habit, even though one may possess the material in large quantities; but, under all circumstances, let it be a fixed rule never to use up all one has of a substance, but always to keep a portion of it, even though a small one, for unforeseen contingencies, and for confirmatory experiments.

* Do not fail to consult the observations in the Third Section of Part II.

† These marginal numbers are simply intended to facilitate reference.

A. The Substance under Examination is Solid.

I. It is neither a Metal nor an Alloy.

§ 211.

1. The substance is fit for examination if in powder or in minute crystals; but in the case of larger crystals or solid pieces, a portion must, if practicable, be first reduced to *fine powder*. Bodies of the softer kind may be triturated in a porcelain mortar; while those of a harder nature must first be broken into small pieces in a steel mortar, or upon a steel anvil, and the pieces then triturated in an agate mortar. 2

2. Put some of the powder into a glass tube, sealed at one end, about 7 cm long and 5 mm wide, or else in a glass tube blown out to a small bulb at the end, and heat first gently over the spirit- or gas-lamp, then intensely in a gas flame, the heat of which is increased by a chimney, or in the blowpipe flame. The reactions resulting may lead to many positive or probable conclusions regarding the nature of the substance. The following are the most important of these reactions, to which particular attention ought to be paid; and it often occurs that several of them are observed in the case of one and the same substance: 3

a. The substance remains unaltered: absence of organic matters, salts containing water of crystallization, readily fusible matters, and volatile bodies (except carbon dioxide, which often escapes without visible change).

b. The substance changes color but does not fuse at a moderate heat: from white to yellow, turning white again on cooling, indicates zinc oxide; from white to yellowish-brown, turning to a dirty 4

light yellow on cooling, indicates STANNIC OXIDE; from white or yellowish-red to brownish-red, turning to yellow on cooling, the body fusing at a red heat, indicates LEAD OXIDE; from white or pale yellow, to orange-yellow, up to reddish-brown, turning pale yellow on cooling, the body fusing at an intense red heat, indicates BISMUTH OXIDE; from white or yellowish white to dark brown, remaining dark brown upon cooling, indicates MANGANOUS OXIDE (*e.g.*, manganous carbonate), but when becoming (usually) light reddish-brown on cooling, indicates CADMIUM OXIDE (*e.g.*, cadmium carbonate); from light blue or light green to black, water being given off at the same time, indicates CUPRIC OXIDE (cupric hydroxide or carbonate), and also the corresponding NICKEL COMPOUNDS; from grayish-white to black indicates FERROUS CARBONATE; from brownish-red to black, turning brownish-red again on cooling, indicates FERRIC OXIDE; from yellow to dark orange, the body fusing at an intense heat, indicates POTASSIUM CHROMATE; from light red to dark red then violet-black, becoming light red again on cooling, giving a sublimate of mercury upon stronger ignition, allows the recognition of MERCURIC OXIDE; from light red to brown, light red upon cooling, RED OXIDE OF LEAD, which gives yellow, fusible lead oxide when intensely heated, etc.

c. THE SUBSTANCE FUSES WITHOUT EXPULSION OF AQUEOUS VAPORS. If, by intense heating, a gas (oxygen) is evolved, and a small fragment of charcoal thrown in is energetically consumed, NITRATES or CHLORATES are indicated. 5

d. AQUEOUS VAPORS ARE EXPELLED, WHICH CONDENSE IN THE COLDER PART OF THE TUBE: this indicates either (α) SUBSTANCES CONTAINING WATER OF CRYSTALLIZATION, in which case they generally fuse readily, and resolidify after expulsion of the water (many of these swell considerably while yielding up their water, *e.g.*, borax, alum); (β) decomposable HYDROXIDES, or SALTS CONTAINING CHEMICALLY COMBINED WATER in which case the bodies often do not fuse; (γ) anhydrous salts, 6

aa. SULPHUR: this is given off from mixtures or from many of the metallic sulphides. It sublimes in reddish-brown drops, which solidify on cooling, and turn yellow or yellowish-brown.

bb. IODINE: this escapes from mixtures, many iodides, iodic acid, etc. It gives a violet vapor, black sublimate, and smell of iodine.

cc. AMMONIUM SALTS give white sublimates; and when heated with sodium carbonate and a drop of water on platinum foil, they evolve ammonia.

dd. MERCURY and its compounds. METALLIC MERCURY forms globules; MERCURIC SULPHIDE is black, but acquires a red tint when rubbed; MERCURIC CHLORIDE fuses before volatilizing, and gives a white sublimate; MERCUROUS CHLORIDE sublimes without previous fusion, the sublimate, which is yellow while hot, turning white on cooling; and red MERCURIC IODIDE gives a yellow sublimate.

ee. ARSENIC and its compounds. METALLIC ARSENIC forms the well-known arsenical mirror; ARSENIOUS OXIDE forms small, brilliant crystals; the SULPHIDES OF ARSENIC give sublimates which are reddish-yellow while hot, and turn yellow or yellowish-red on cooling.

ff. ANTIMONIOUS OXIDE fuses to a yellow liquid before subliming. The sublimate consists of brilliant needles.

gg. LEAD CHLORIDE fuses to a yellow liquid before forming a sublimate. The latter is white and difficultly volatile.

hh. BENZOIC and SUCCINIC ACIDS give white, crystalline sublimates. The officinal, slightly impure acids may be known by the odor of their fumes.

ii. SALICYLIC ACID gives a white, crystalline sublimate. Upon heating quickly and intensely, there is an odor of phenol.

kk. OXALIC ACID gives a white, crystalline sublimate, with thick, irritating fumes in the tube, which produce coughing. Heating a small sample on plati-

num foil with a drop of concentrated sulphuric acid gives rise to a copious evolution of gas.

h. CARBONIZATION TAKES PLACE: organic substances. 10
This is always attended with evolution of gases (acetates evolve acetone) and water, the latter having an alkaline or acid reaction. An odor like burnt hair indicates nitrogenous organic substances. If the residue effervesces with acids, while the original substance did not show this reaction, organic acids may be assumed to be present in combination with alkali or alkali-earth metals. Salts containing readily reducible metals in combination with organic acids (*e.g.*, cupric acetate) often leave the metal behind, and in consequence of this (*i.e.*, in consequence of the combustion of the carbon at the expense of the oxygen of the metallic oxide), little or no carbon remains.

3. PLACE A SMALL PORTION OF THE SUBSTANCE ON CHAR- 11
COAL (in a cavity scooped out for the purpose), AND EXPOSE IT TO THE INNER BLOWPIPE FLAME.

As most of the reactions which take place in heating in the closed glass tube are also produced by this process, only those will be mentioned which are peculiar to this experiment. Evolution of sulphur dioxide, when the flame plays upon the substance on charcoal, generally indicates sulphur or a sulphide. If a garlic-like odor of arsenic is given off, this indicates arsenic or an arsenic compound. If there is an odor of ammonia, this points to certain ammonium compounds (*e.g.*, ammonium carbonate). If a lively combustion of the charcoal takes place, the substance is one which gives off oxygen, generally a nitrate or a chlorate. In the case of substances which have given sublimates in the glass tube, one should avoid breathing the vapors which are evolved.

In addition to the above, the following reactions will permit moderately accurate conclusions:

a. THE BODY FUSES, AND IS ABSORBED BY THE CHAR- 12
COAL, OR FORMS A BEAD IN THE CAVITY, not attended by incrustation: this indicates more particularly salts of the alkali metals.

b. AN INFUSIBLE, WHITE RESIDUE REMAINS on the charcoal, either at once or after previous melting in water of crystallization: this indicates more particularly the oxides of barium, strontium, calcium, magnesium, aluminium, zinc (appears yellow while hot), and silicic oxide. Among these substances, the OXIDES of STRONTIUM, CALCIUM, MAGNESIUM, and ZINC, are distinguished by strong luminosity in the blowpipe flame; and the oxides of the alkali-earth metals, by the fact that they react alkaline, as do also their sulphides. Moisten the white residue with a drop of cobalt nitrate solution, and expose again to a strong heat. Many colorations are thus produced, of which the following are especially characteristic and are distinctly perceptible: A fine blue tint indicates ALUMINA or SILICA; a green color shows ZINC OXIDE; while violet indicates MAGNESIUM PHOSPHATE and also MAGNESIUM ARSENATE. In the presence of many PHOSPHATES of the alkali-earth metals, a more or less blue coloration is produced, a fact which is to be heeded. 13

In the case *a* or *b*, the preliminary examination for alkali and alkali-earth metals may be completed by inspecting the colors which the substances impart to the flame. For this purpose, a little of the substance is attached to the loop of a fine platinum wire, moistened with hydrochloric acid, dried cautiously near the border of the flame, moistened again with hydrochloric acid, and then held in the fusing zone of a BUNSEN gas flame. The colorations caused by the alkali metals make their appearance first, followed, after volatilization of the alkali metals, by those of barium, strontium, or calcium. Sometimes it is advisable first to ignite the sample in the reducing flame, and after that to moisten it with hydrochloric acid, *e.g.*, if sulphates are under investigation. For details, see §§ 17, 97, and 104.

c. THE SUBSTANCE LEAVES A RESIDUE OF ANOTHER COLOR, OR REDUCTION TO THE METALLIC STATE TAKES PLACE, OR A COATING FORMS ON THE CHARCOAL. In this case do not draw a conclusion directly from the 14

reaction which has taken place, but in order to produce more decisive results mix a portion of the powder with sodium carbonate and a drop of water (an odor of ammonia occurring here shows the presence of an ammonium compound), heat on charcoal in the reducing flame, and observe the residue in the cavity as well as the incrustation on the charcoal. If a sulphide or arsenide is under investigation (see 11), or if the substance was rich in water of crystallization, heat it, in the first place, for a short time on the cover of a porcelain crucible, pulverize the residue, and then mix it with sodium carbonate.

α. The sustained application of a strong flame 15
produces a metallic globule, without incrustation of the charcoal: this indicates GOLD or COPPER. The latter is at once recognized by the green coloration of the flame. The compounds of platinum, iron, cobalt, and nickel, are also reduced, but if pure, they yield no metallic globules.

β. The charcoal support is coated with an in- 16
crustation, either with or without the formation of a metallic globule.

aa. The incrustation is *white*, forms at some distance from the test specimen, and is very readily dissipated by heat, emitting a garlic-like odor: ARSENIC.

bb. The incrustation is *white*, is nearer the test specimen than in *aa*, and may be driven from one part of the support to another: ANTIMONY. Metallic globules are generally observed at the same time, which continue to evolve white fumes long after the blowpipe flame is removed, and upon cooling, become surrounded with crystals of antimonious oxide. The globules are brittle.

cc. The coating is *yellow* while hot, but turns white on cooling, is rather near the test specimen, is volatilized with difficulty, and gives a green coloration when ignited with cobalt nitrate: ZINC.

dd. The incrustation has a *faint yellow* tint while hot, but turns white on cooling. It sur-

rounds the test specimen closely, and both the inner and outer flame fail to volatilize it: TIN. The metallic globules formed at the same time, but only in a strong reducing flame, are bright, readily fusible, and malleable.

ee. The coating has a *lemon-yellow* color, turning to sulphur-yellow on cooling. When heated in the reducing flame, it volatilizes, tingeing the flame blue: LEAD. Readily fusible, malleable globules are formed at the same time.

ff. The coating while hot is of a *dark orange-yellow* color, which changes to lemon-yellow on cooling; and when heated in the reducing flame, it changes its place without coloring the flame blue: BISMUTH. The metallic globules formed at the same time are readily fusible and brittle.

gg. The coating is *reddish-brown*, or in thin layers, *orange-yellow*. It volatilizes without coloring the flame: CADMIUM.

hh. The incrustation is slight and *dark red*, while white, metallic globules are formed: SILVER. Where a little lead and antimony are present at the same time, the incrustation is crimson.

If only an incomplete reduction of metal has been obtained, it is advisable to repeat the experiment, adding a little potassium cyanide to the mixture of the sample with sodium carbonate, or mixing the sample with sodium formate, because in this way, the metallic reductions are greatly facilitated.

If the reduction of a metal has taken place, the sample should be moistened with water, and, with the surrounding charcoal, cut out, triturated in a small agate mortar, and the particles of charcoal carefully washed away. Any metal that may be present remains in the mortar, gold in yellow, copper in red, silver in almost white, tin in grayish-white, lead in whitish-gray, scales or streaks. Bismuth will remain as a reddish-gray, zinc a bluish-gray, and antimony a gray, powder.

When copper and tin or copper and zinc are simultaneously present, yellow alloys of these metals may be formed.

γ. If sodium sulphide has been produced (the detection of which is easily accomplished according to § 170, 6), the presence of a sulphide, a sulphate, or perhaps a sulphite, is shown. 17

4. FUSE A SMALL PORTION WITH A BEAD OF SODIUM METAPHOSPHATE (see § 89), AND EXPOSE FOR SOME TIME TO THE OXIDIZING GAS OR BLOWPIPE FLAME.

a. THE SUBSTANCE DISSOLVES READILY AND COPIOUSLY TO A CLEAR BEAD (WHILE HOT).

α. *The hot bead is colored*— 18

BLUE, which by candlelight inclines to violet: COBALT.

GREEN, but upon cooling, blue; in the reducing flame, but only when strongly saturated, after cooling, red: COPPER.

GREEN, particularly fine on cooling, unaltered in the reducing flame: CHROMIUM.

BROWNISH-RED, but on cooling, light yellow or colorless; in the reducing flame, red while hot, yellow while cooling, then greenish: IRON.

REDDISH TO BROWNISH-RED, but on cooling, paler, yellow to reddish-yellow or even colorless; in the reducing flame, unaltered: NICKEL.

YELLOWISH-BROWN, but on cooling, light yellow or colorless; in the reducing flame, almost colorless (especially after addition of a very little tin), and blackish-gray on cooling: BISMUTH.

LIGHT YELLOWISH to OPAL, but when cold, rather turbid; in the reducing flame, whitish-gray: SILVER.

AMETHYST-RED, especially on cooling; colorless, and not quite clear in the reducing flame: MANGANESE.

β. The hot bead is colorless. 19

aa. IT REMAINS CLEAR ON COOLING: ANTIMONY, ALUMINIUM, ALKALI-METALS, ZINC, CADMIUM, LEAD, CALCIUM, MAGNESIUM. The last five, when added in somewhat large proportion to the sodium metaphosphate, give enamel-white beads; while the bead saturated with lead oxide is yellowish.

bb. IT BECOMES ENAMEL-WHITE ON COOLING, EVEN WHERE ONLY A SMALL PORTION OF THE POWDER HAS BEEN ADDED TO THE SODIUM METAPHOSPHATE: BARIUM, STRONTIUM.

b. THE SUBSTANCE DISSOLVES SLOWLY AND ONLY IN SMALL QUANTITY. 20

α. The bead is colorless, and remains clear even after cooling; the undissolved portion looks semi-transparent; and upon the addition of a little ferric oxide, it acquires the characteristic color of an iron bead: SILICIC OXIDE.*

β. The bead is colorless, and remains so after the addition of a little ferric oxide: TIN.

c. THE SUBSTANCE DOES NOT DISSOLVE, BUT FLOATS (IN THE METALLIC STATE) IN THE BEAD: GOLD, PLATINUM. 21

5. MINERALS ARE EXAMINED FOR FLUORINE AS DIRECTED IN § 176, 8.

As the body under examination may consist of a mixture of the most dissimilar substances, the statement of cases with entirely sharp limits is not possible under all circumstances in connection with these tests. If, therefore, reactions which proceed from a combination of two or several cases are observed in an experiment, they must of course be interpreted accordingly.

After the termination of the preliminary examination, proceed to the solution of the substance, as directed in § 215 (32).

* In regard to the behavior of silicates in the sodium metaphosphate bead, compare K. HAUSHOFER, also J. HIRSCHWALD, Zeitschr. f. analyt. Chem., 29, 318.

§ 212.

II. The Substance is a Metal or an Alloy.

1. Heat a small portion of the substance with water acidified with acetic acid. If hydrogen is evolved, this indicates a light metal (possibly also manganese). 22

2. Heat a sample on charcoal in the reducing flame of the blowpipe, and observe whether the substance fuses, whether a coating is formed, or an odor emitted, etc. 23

By this operation, the following metals may be detected with more or less certainty: arsenic by the smell of garlic; mercury by its volatility; antimony, zinc, lead, bismuth, cadmium, tin, silver, by fusing, with coating of the charcoal (compare **16**); copper by the green coloration of the outer flame. Further conclusions may be reached when the substance is a single metal nearly or quite pure; for instance, gold fuses without forming a coating; while platinum, iron, manganese, nickel, and cobalt, when pure, do not fuse in the blowpipe flame.

3. Heat a sample of the substance before the blowpipe in a glass tube closed at one end. 24

a. No sublimate is formed in the colder part of the tube: absence of mercury.

b. A sublimate is formed: presence of mercury, cadmium, or arsenic. The sublimate of mercury, which consists of small globules, cannot be easily confounded with that of cadmium or arsenic. The fact that a sublimate is not formed, however, does not justify the conclusion that cadmium and arsenic are not present.

After the termination of the preliminary examination, proceed to the solution of the substance, as directed in § 217 (**42**).

§ 213.

B. THE SUBSTANCE UNDER EXAMINATION IS A LIQUID.

1. EVAPORATE A SMALL PORTION OF THE LIQUID in a plati- 25
num capsule, or in a small porcelain crucible, to ascertain whether it actually contains any matter in solution; and if a residue remains, examine this as directed in § 211.

2. TEST WITH LITMUS-PAPER (blue and red).

a. THE LIQUID REDDENS BLUE LITMUS-PAPER: this 26
reaction may be caused by a free acid or an acid salt, as well as by normal salts of the heavy metals, soluble in water. To distinguish between these two cases pour a small quantity of the liquid into a watch-glass, and dip into it a small glass rod, after moistening the extreme point of the latter with dilute solution of sodium carbonate. If the liquid remains clear, or if the precipitate which may form at first redissolves upon stirring the liquid, this proves the presence of a free acid or of an acid salt; but if the fluid becomes turbid and remains so, this generally denotes the presence of a soluble salt of a heavy metal.

b. REDDENED LITMUS-PAPER TURNS BLUE: this indi- 27
cates the presence of an alkali or alkali-earth metal in the state of hydroxide, sulphide, or (alkali metal) carbonate, as well as a series of other salts of the alkali and alkali-earth metals with weak acids (among the compounds containing heavy metals, only a few lead salts, *e.g.*, basic lead acetate, and also the solutions of thallous hydroxide and carbonate, give an alkaline reaction).

3. SMELL THE FLUID, or, should this fail to give satis- 28
factory results, DISTIL, to ascertain whether the simple solvent present is water, alcohol, ether, etc. If it is not water, evaporate the solution to dryness, and treat the residue as directed in § 211.

4. If the solution is aqueous, and manifests an acid 29
reaction, DILUTE A PORTION OF IT LARGELY WITH WATER.

Should this impart a milky appearance to it, the presence of ANTIMONY or BISMUTH (or possibly also of tin or lead) may be inferred. (Compare § 141, 9, and § 154, 4.)

On completing the preliminary examination of a 30
liquid, the operator may proceed to its actual analysis. If the solution is aqueous and *reacts neutral*, only bodies which are soluble in water can be present. On the contrary, if it has an *acid reaction*, in consequence of the presence of a free acid, it can no longer be considered simply aqueous, and the analysis must be conducted with regard to the possible presence of substances insoluble in water, but soluble in acids. Bearing in mind these considerations, the operator passes on, if the assumption is warranted that only one base and one acid are present, to §§ 218 and 219 or 220, or, as the case may be, to §§ 221 and 222 or 223. If, however, the above assumption cannot be made, he should proceed according to §§ 225 and 235 or 236, or, as the case may be, 237 or 238. If liquids react alkaline, §§ 218 and 219 or 220 should be followed, if it may be assumed that only a single base and acid are present, and in the other case, §§ 225 and 235 or 236, or, if the case demands it, 237 or 238.

II. SOLUTION OF BODIES, OR CLASSIFICATION OF SUBSTANCES ACCORDING TO THEIR DEPORTMENT WITH CERTAIN SOLVENTS.*

§ 214.

Water and acids (hydrochloric acid, nitric acid, aqua 31
regia) are the solvents used to classify simple or compound substances, and to isolate the component parts of mixtures. We divide substances into three classes, according to their respective deportment with these solvents, as follows:

First class.—SUBSTANCES SOLUBLE IN WATER.

Second class.—SUBSTANCES INSOLUBLE OR SPARINGLY SOLUBLE IN WATER, BUT SOLUBLE IN HYDROCHLORIC ACID, NITRIC ACID, OR AQUA REGIA.

* Consult the remarks in the Third Section.

Third class.—SUBSTANCES INSOLUBLE OR SPARINGLY SOLUBLE IN WATER, AS WELL AS IN HYDROCHLORIC ACID, NITRIC ACID, OR AQUA REGIA.

The solution of metals and alloys being more appropriately effected in a somewhat different manner from that pursued with other bodies, a special method will be given for these substances (see § 217).

The process of solution is conducted in the following manner:

A. THE SUBSTANCE UNDER EXAMINATION IS NEITHER A METAL NOR AN ALLOY.

SIMPLE COMPOUNDS.*

§ 215.

If a simple compound is to be examined, find in 32
which class it belongs in regard to solubility. For this purpose treat a small portion with distilled water, then if necessary with dilute hydrochloric acid, concentrated hydrochloric acid, nitric acid, and aqua regia, in the order in which they are here given, first without, and then with, the application of heat. If the small sample is brought into solution by one of the solvents, treat a somewhat larger portion (about 1 g) in the same manner, and proceed with aqueous solutions according to §§ 218 and 219 or 220; with acid solutions by §§ 221 and 222 or 223; and with bodies insoluble or difficultly soluble in acids according to § 224.

The phenomena which may occur in the treatment 33
with HYDROCHLORIC ACID, and which must be carefully noticed, are—

α. Effervescence, indicating carbonic acid or hydrogen sulphide.

β. Evolution of chlorine, indicating peroxides, chromates, etc.

γ. Evolution of an odor of hydrocyanic acid, indicating cyanides insoluble in water (since the latter are

* This name is selected for the sake of brevity, and is used here and beyond for those compounds in which only *one* base and *one* acid, or *one* metal and *one* non-metal, are assumed to be present.

more conveniently decomposed in a different manner, a special section is devoted to them; see § 240).

In the treatment with NITRIC ACID, the evolution of nitric oxide (the appearance of red fumes) indicates that a process of oxidation is taking place. If the substance dissolves in ACIDS, with separation of sulphur (to be recognized by its appearance, color, and specific gravity, and may be separated by filtration after long boiling), or of silicic acid, usually gelatinous, a sulphide or a silicate decomposable by acids is present. The solution, filtered after dilution,* is then to be investigated by § 221; and the precipitate remaining undissolved and filtered off may be tested further according to § 224.

COMPLEX COMPOUNDS.†

§ 216.

If a complex compound is the object of investigation, 34
it is advisable at first, if necessary, to separate the substances from each other according to their solubilities. For this purpose proceed as follows:

1. Put about 1 to 3 g of the pulverized substance into a flask, add about ten times its amount of distilled water, and heat to boiling over a spirit- or gas-lamp.

a. A CLEAR SOLUTION IS OBTAINED. In this case, all 35
its constituents belong to the first solubility-class, and attention must be paid to what has been stated in the preliminary examination (30) with respect to the reaction. For the determination of the metals proceed according to § 225; for the acids, according to § 235, or, if the case requires it, § 236.

b. AN INSOLUBLE RESIDUE REMAINS, EVEN AFTER PRO- 36
TRACTED BOILING. Let the residue subside, and filter the fluid off, if practicable, in such a manner as to

*A turbidity produced by this dilution indicates bismuth or antimony (possibly also tin or lead). A turbidity caused by the first two may be removed by the addition of hydrochloric acid.

†By these are meant, both here and beyond, compounds or mixtures in which all the commonly occurring bases, acids, metals, and non-metals may be present.

retain the residue in the flask; then evaporate a few drops of the clear filtrate in a platinum or porcelain dish. If nothing remains, the substance is completely insoluble in water, in which case proceed as directed at 37; but if a residue remains, constituents of the substance are soluble in water. Boil repeatedly with water in order to bring the constituents soluble in that liquid as completely as possible into the aqueous solution,* and then proceed with this as given in 35, but with the undissolved residue according to 37.

2. Treat a portion of the substance which is insoluble in water, or the residue which has been extracted with water as far as possible, with dilute HYDROCHLORIC ACID. If it does not dissolve, or does not dissolve completely, heat to boiling, and if this fails to effect complete solution, decant the fluid into another flask, boil the residue with concentrated hydrochloric acid, and, if it dissolves, add the solution to that which was poured off. 37

Concerning the reactions which may manifest themselves in this treatment with hydrochloric acid, compare 33.

a. THE SUBSTANCE IS COMPLETELY DISSOLVED BY THE HYDROCHLORIC ACID (except perhaps that sulphur or gelatinous silicic acid separates; compare 33). The substance insoluble in water (or the proximate constituents of it) belongs to the second class in regard to solubility. Go on to § 226. Any separated sulphur or silicic acid is to be tested, if necessary, by § 239. 38

b. THERE IS STILL A RESIDUE LEFT. In this case put aside for the present the flask containing the sample which has been boiled with the hydrochloric acid, and go on to 39.

3. If hydrochloric acid has not completely dissolved the substance insoluble in, or extracted as far as possible with, water, try to dissolve another portion of it by heating with NITRIC ACID and adding water afterwards. 39

* If substances difficultly soluble in water are present (*e.g.*, calcium sulphate or lead chloride), one should be satisfied with boiling four times, because, in this case, a complete exhaustion with water is difficult to attain.

Concerning the phenomena which may take place during this treatment, compare 33.

a. COMPLETE SOLUTION TAKES PLACE BY TREATMENT WITH NITRIC ACID (or only sulphur or silicic acid separate; compare 33). In this case, also, the substance insoluble in water, or the proximate constituents of it, belong to the second solubility-class. Proceed with the nitric acid solution by § 225, III., 109, and otherwise as directed in 38.

b. THERE IS STILL A RESIDUE LEFT UPON HEATING WITH NITRIC ACID. Pass on to 40.

4. If the residue insoluble in water will not entirely 40
dissolve in hydrochloric acid nor in nitric acid, try to effect complete solution of it by means of AQUA REGIA (nitro-hydrochloric acid). To this end, mix the contents of the flask treated with nitric acid with the contents of that treated with concentrated hydrochloric acid, heat the mixture slowly at last to gentle boiling, and should this fail to effect complete solution, decant off the clear fluid from the undissolved residue, heat the latter for some time with concentrated nitro-hydrochloric acid, and then add the decanted solution of dilute aqua regia, as well as the solution in dilute hydrochloric acid decanted in 37. Heat the entire mixture once more to boiling, and observe whether complete solution has now been effected, or whether the action of the concentrated nitro-hydrochloric acid has still left a residue. In the *latter* case filter the solution—if necessary, after addition of some water *—wash the residue with boiling water, and proceed with the filtrate and the washings added to it, as directed in § 226. In the *former* case proceed with the clear solution in the same way.†

* If the liquid turns turbid upon addition of water, this usually indicates the presence of bismuth or antimony; but the turbidity will disappear upon addition of hydrochloric acid.

† Where the acid solution on cooling deposits acicular crystals, the latter generally consist of lead chloride. In that case, it is often advisable to decant the fluid from the crystals, and to examine each part separately. Where on boiling with aqua regia metastannic chloride has been formed, the washing water dissolving this becomes turbid on dropping into the strongly acid fluid which has run off first. In that case receive the washing water in a

5. If boiling nitro-hydrochloric acid has left an undis- 41
solved residue, wash it thoroughly with boiling water, and then proceed with it as directed in § 239.

B. The Substance under Examination is a Metal or an Alloy.

§ 217.

The metals are best classed according to their behavior 42
with nitric acid, as follows:

I. Metals which are not attacked by nitric acid: gold, platinum.

II. Metals which are oxidized by nitric acid, but whose oxides do not dissolve (in any considerable amount) in an excess of the acid or in water: antimony, tin.

III. Metals which are oxidized by nitric acid and converted into nitrates, which dissolve in an excess of the acid or in water: all the other metals.

Since the chemically pure, reguline metals are only very seldom the object of qualitative analysis (for almost all the commercial metals are not chemically pure, but contain smaller or larger amounts of other elements), I shall not give separately here methods for treating metals and alloys, but shall consider the latter only, because the process will then be suitable under all circumstances, whether actual alloys, impure metals, or even pure metals are under examination. As far as the amounts to be treated with nitric acid are concerned, very small portions suffice for pure metals; while for the determination of the essential constituents of alloys (that is, their analysis where small amounts of metals occurring as impurities are not taken into account), 1 to 3 g suffice. If, however, it is a question of finding the metallic impurities, usually occurring only in traces, in metals produced by metallurgical processes (*e.g.*, testing soft lead for bismuth, copper, antimony, iron, zinc, silver, etc.), amounts as large as 100 to 200 g must be operated upon.

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separate vessel, and treat the two solutions separately with hydrogen sulphide, as directed in § 226, but filter afterwards through the same filter.

Heat the sample with nitric acid of 1.2 sp. gr., to which an equal volume of water is added if lead nitrate separates.

1. COMPLETE SOLUTION TAKES PLACE, EITHER AT ONCE OR UPON ADDITION OF WATER: this proves the absence of platinum,* gold, antimony,† and tin. As the case demands, only one or several metals being assumed to be present, proceed according to § 221 or § 225, III., **109**. 43

2. A RESIDUE IS LEFT. Filter this off, and after having tested to find if anything at all was dissolved, proceed with the filtrate, according to § 225, III., **109**.

a. The residue *is metallic.* Dissolve it in aqua regia, and test the solution for GOLD and PLATINUM by § 151. 44

b. The residue is *white* and *pulverulent:* this generally indicates ANTIMONY or TIN. If the case warrants the assumption that only one or the other of these metals is present, it is sufficient to fuse the washed and dried residue with sodium carbonate and some potassium cyanide, or with sodium formate in a cavity on charcoal in the reducing flame of the blowpipe, in order to see whether a ductile tin bead or a brittle one of antimony is obtained. But if several metals may be present, the case becomes more complicated, since bismuth arsenate is difficultly soluble in nitric acid; and lead oxide, copper oxide, and other metallic oxides may remain behind with the antimonic acid and the metastannic acid. In this case, it is best to fuse the washed and dried residue in a porcelain crucible, kept well covered, with about four parts of a mixture of equal parts of sodium carbonate and sulphur, then to let the mass cool, and treat it with water. If a residue remains, filter and wash it, then dissolve it in nitric acid, and test the solution according to § 225, III., **109**, for the metals of the fifth and fourth groups. The yellow alkaline

* Alloys of silver and platinum, with the latter metal present in small proportion only, dissolve in nitric acid.

† Very minute traces of antimony, however, are often completely dissolved by nitric acid.

solution, on the other hand, is acidified with hydrochloric acid, the metals of the sixth group are thus precipitated, and the washed precipitate is examined by § 228.

c. The residue is a *white, flocculent* one: this indi- 45
cates separated SILICIC ACID, but since the heavy-metal compounds mentioned in *b* may be mixed with it, treat in the first place a well-washed portion of it in a cavity on charcoal with sodium carbonate and potassium cyanide or with sodium formate, by which means the heavy metals may be detected. If these are present, fuse the remainder of the residue as directed in *b* with sodium carbonate and sulphur, obtaining the silicic acid in solution. If the solution, sufficiently diluted, is acidified with hydrochloric acid, the sulphides of the sixth group (to be examined by § 228) are filtered off, the liquid is evaporated to dryness, and the residue is treated with hydrochloric acid, the silicic acid remains undissolved (§ 180, 2).

d. The residue is a *black* one: this indicates separated CARBON. Test a portion in the first place, to find if it is completely consumed when heated strongly and persistently upon platinum foil. If a residue remains, examine it according to *a*, *b*, or *c*, as its properties may indicate.

III. Actual Analysis.

*Simple Compounds.**

A. Substances soluble in Water.

Detection of the Metal.†

§ 218.

1. Add a little hydrochloric acid to a part of the not too concentrated aqueous solution. If the liquid reacts alkaline, hydrochloric acid must be added to distinct acid reaction. 46

a. No precipitate results: the absence of silver and mercurous salts is indicated, as well as the absence of any considerable quantity of lead. Pass on to **50**.

b. A precipitate is formed, which is not dissolved upon the addition of more hydrochloric acid.‡ Divide the liquid in which it is suspended 47

* As has been mentioned above, this term is used for the sake of brevity, both here and subsequently, for those compounds in which it is assumed that only *one* base and *one* acid, or *one* metal and *one* non-metal, are present. The salts are usually to be considered as *normal*. The present section has the special aim of facilitating instruction in analysis, since it is advisable that the analysis of simple compounds should precede that of complex bodies. In actual analysis, only exceptional use can be made of this section, because there is no external criterion which indicates whether a body contains only one base or acid or whether it contains several.

† In this course, arsenious acid, arsenic acid, and silicic acid are taken into consideration, because their detection takes place conveniently here.

‡ Besides silver chloride, mercurous chloride, and lead chloride, as well as basic antimony salts and basic bismuth chloride (the basic salts, however, dissolve in a small excess of hydrochloric acid), the precipitate by hydrochloric acid may contain silicic acid if the solution was concentrated and had a strong alkaline reaction. Moreover, if the solution was concentrated, the precipitate may possibly contain also barium chloride and metastannic chloride, and further, if the preliminary examination has shown the presence of organic substances, benzoic or salicylic acid may be precipitated. The silicic acid precipitate is gelatinous; while barium chloride, benzoic acid, and salicylic acid are crystalline. The precipitates of barium chloride, metastannic chloride, silicic, benzoic, and salicylic acids will not be obtained if the solution is sufficiently diluted with water, and hydrochloric acid is added only in small amount.

into two parts, and to one of them add ammonia in excess.

α. The precipitate disappears, and the liquid becomes clear. In this case, it was silver chloride, and the presence of SILVER is shown. For confirmation, test the original solution with potassium chromate and with hydrogen sulphide (see § 135, 8 and 4).

β. The precipitate becomes black. In this case, it 48
was mercurous chloride, which is decomposed by ammonia (§ 136, 6). By this, the presence of (mercurous) MERCURY is recognized. For confirmation, test the original solution with stannous chloride and with metallic copper (§ 136, 7 and 8).

γ. The precipitate remains unchanged. In this 49
case, it is lead chloride, which is not dissolved by ammonia. The presence of LEAD is shown by this. Confirm by diluting the other half of the solution, in which the precipitate produced by hydrochloric acid is suspended, with much water and boiling. The precipitate must dissolve if it is really lead chloride. Confirm further by testing portions of the original solution with hydrogen sulphide and with sulphuric acid (§ 137, 4 and 8).

2. Add hydrogen sulphide water to the solution which 50
is acidified with hydrochloric acid, until it smells distinctly of hydrogen sulphide even after shaking, heat the liquid, add more hydrogen sulphide water, and let it stand for a short time.*

a. THE LIQUID REMAINS CLEAR. Pass on to **56**, for lead, bismuth, copper, cadmium, mercury (in mercuric salts), gold, platinum, tin, antimony, arsenic, and iron (in ferric compounds) are not present.

b. A PRECIPITATE IS OBTAINED.

α. THE PRECIPITATE IS WHITE. In this case, it is 51

* If a precipitate is formed at once upon the addition of hydrogen sulphide water, the heating, etc., is not necessary; but if the liquid remains clear or becomes only slightly turbid, the above process must be strictly followed, for otherwise there is danger that arsenic acid and stannic salts may be overlooked.

due to sulphur, and indicates a substance which decomposes hydrogen sulphide, with the separation of sulphur.* Ferric salts most commonly produce this separation of sulphur (§ 127, 3). Test for them in the original solution with potassium ferrocyanide (§ 127, 6). If a ferric salt is not found, and if a change of color of the solution did not lead to the conclusion that chromic acid or hydroferricyanic acid were present (see foot-note), pass on to **56**.

β. THE PRECIPITATE IS YELLOW. This may be **52** cadmium sulphide, sulphide of arsenic, or stannic sulphide, and therefore indicates the presence of cadmium, arsenic, or tin (stannic). To distinguish these cases, add ammonia in excess to a portion of the liquid in which the precipitate is suspended, then add a little ammonium sulphide, and warm.

αα. It does not disappear: CADMIUM, for cadmium sulphide is insoluble in ammonia and ammonium sulphide. Confirm by testing the original substance or the precipitate thrown down from the solution by ammonium carbonate, by means of the blowpipe (§ 142, 9).

bb. It disappears: TIN (stannic) or ARSENIC. Add sodium carbonate to a part of the original solution.

αα. A white precipitate is formed: STANNIC OXIDE. Confirm by reduction of the precipitate with sodium carbonate and potassium cyanide or with sodium formate before the

* In this reaction, if the color of the solution changes from reddish-yellow to green, this indicates chromic acid, but if it gradually changes from yellow to light blue, hydroferricyanic acid is indicated. In the first case, two bases are therefore in solution after the action of hydrogen sulphide, chromic oxide, and the base which had been combined with the chromic acid, and one should proceed as in § 230. In the second case, moisten the dry substance, or the residue obtained by evaporating the aqueous solution, with some concentrated sulphuric acid, heat under a good draught-hood until the greater part of the sulphuric acid has escaped, dissolve the residue in water, and proceed with the solution, which now contains ferric sulphate derived from ferricyanogen in addition to the sulphate of the base originally present, according to § 230.

blowpipe (§ 153, 11), or by testing the original solution with ammonium nitrate (§ 153, 8).

ββ. No precipitate is formed: ARSENIC. If the solution contained arsenious acid, the yellow precipitate was immediately formed by hydrogen sulphide. Confirm by testing the original solution by § 155, 6 and 8. If it contained arsenic acid, the precipitate was produced by hydrogen sulphide only after warming, or standing for some time. Confirm according to § 156, 5 and 9.

γ. THE PRECIPITATE HAS AN ORANGE COLOR. It 53
is antimony sulphide, and indicates ANTIMONY. Confirm this by testing the original solution with zinc in a platinum dish (§ 154, 9), and determine in which state of oxidation the antimony is present by § 157, 11.

δ. THE PRECIPITATE IS DARK BROWN. In this 54
case, it is stannous sulphide, and shows the presence of a STANNOUS SALT. For confirmation, test a small part of the original solution with mercuric chloride (§ 152, 9).

ε. THE PRECIPITATE IS BROWNISH-BLACK OR BLACK. 55
It may then be lead sulphide, copper sulphide, bismuth sulphide, gold sulphide, platinum sulphide, or mercuric sulphide. To distinguish these cases, make the following experiments with the original solution:

aa. To a part, add dilute sulphuric acid. White precipitate: LEAD. Confirm with potassium chromate (§ 137, 9).

bb. To a portion, add potassium or sodium hydroxide to strong alkaline reaction. Yellow precipitate: MERCURIC OXIDE. Confirm with stannous chloride and with metallic copper (§ 139, 6 and 9).

The presence of a mercuric salt may be usually recognized by the fact that the precipitate which results from the addition of hydrogen sulphide water does not appear black at first, but

changes to this color, only after the addition of an excess of the precipitant, going through white, yellow, and orange to black (§ 139, 3). With *very* acid solutions, the testing with potassium or sodium hydroxide does not give a result (§ 139, 4).

cc. To a part, add ammonia in excess. Bluish precipitate, which dissolves in an excess of ammonia with an azure-blue color, or simply a clear azure-blue liquid: COPPER. Confirm with potassium ferrocyanide (§ 140, 9).

dd. If a white precipitate, which is insoluble in an excess of ammonia, is produced in *cc*, filter it off, wash it, and dissolve a part of it on a watch-glass in one or two drops of hydrochloric acid with the addition of two drops of water, and then add more water. If a milky turbidity results, it is caused by basic bismuth chloride, and therefore shows the presence of BISMUTH. Confirm by testing a few drops of the original solution with a solution of stannous chloride in sodium hydroxide (§ 141, 10).

ee. Add ferrous sulphate solution to a part of the original solution. If a fine, brown precipitate of metallic GOLD is produced, this metal is present. Confirm by treating this precipitate before the blowpipe, or by testing the original solution with stannous chloride (§ 149, 7).

ff. To a part of the solution, concentrated, if necessary, by evaporation, add ammonium chloride and alcohol. If a yellow, crystalline precipitate results, PLATINUM is present. Confirm by igniting the precipitate (§ 150, 6).

3. To a part of the original solution add ammonium 56
chloride,* then ammonia to alkaline reaction, and finally (whether ammonia has produced a precipitate or not) a little ammonium sulphide, and warm gently if no precipitate has been produced in the cold.

* The object of the addition of ammonium chloride is to prevent the precipitation by ammonia of any magnesium that may be present.

a. NO PRECIPITATE IS PRODUCED. Pass on to **62**, for iron, cobalt, nickel, manganese, zinc, chromium, aluminium, and silicic acid are not present.*

b. A PRECIPITATE IS PRODUCED.

α. It is black: iron (ferrous),† nickel, or cobalt. **57**

Mix a portion of the original solution with potassium or sodium hydroxide.

aa. A dirty greenish-white precipitate is obtained, which soon becomes reddish-brown in the air, but upon boiling becomes gray to blackish: FERROUS OXIDE. Confirm with potassium ferricyanide (§ 125, 8).

bb. A light green precipitate is obtained, which does not change its color either in the air or upon boiling: NICKEL. Confirm by ammonia, with the addition of potassium or sodium hydroxide (§ 124, 7).

cc. A sky-blue precipitate is obtained, which becomes light red or also discolored and brownish upon boiling: COBALT. Confirm by the borax bead reaction (§ 125, 16).

β. It is not black.

aa. It is distinctly flesh-red, then it is man- **58**
ganese sulphide, and indicates MANGANESE. Confirm this by adding sodium hydroxide to the original solution, or by fusing the substance with sodium carbonate (§ 123, 6 and 14).

bb. It is bluish-green, and is therefore chromic hydroxide, and indicates CHROMIUM.‡ Confirm

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* This conclusion in regard to aluminium and many of the heavy metals mentioned is certain only when organic substances, especially non-volatile organic acids, are absent, since these may interfere with or prevent the precipitation not only of aluminium and chromium hydroxides, but also that of manganese sulphide, etc. (compare § 123, 5). Therefore, if the original substance contained organic substances, and the preliminary examination has indicated a metal of the third or fourth group, fuse a portion of the substance with sodium carbonate and nitrate, soak out with water, warm with hydrochloric acid, filter, and test the solution thus obtained by **56**.

† Iron in the ferric condition must have been already found in **51**.

‡ Under certain conditions, manganese may precipitate as a green manganese sulphide (§ 123, 5).

this by treating the original solution with sodium hydroxide, or by means of the sodium metaphosphate bead (§ 107, 3 and 11).

cc. It is white, and does not dissolve upon warming with some more ammonium sulphide,* then it may be aluminium hydroxide, hydrated silicic acid, or zinc sulphide, and therefore shows the presence of either aluminium, zinc, or silicic acid, the latter of which generally exists in the form of an alkali-metal silicate in the original solution. To distinguish these, carefully add sodium hydroxide solution to a small part of the original solution, waiting to see whether a precipitate is formed by it, and if necessary add more of the caustic soda until the precipitate has dissolved. 59

αα. If no precipitate was formed by sodium hydroxide, there is reason for testing for silicic acid. Evaporate, therefore, a sample of the original solution to dryness with an excess of hydrochloric acid, and take up the residue with hydrochloric acid and water (§ 180, 2), whereupon the SILICIC ACID remains undissolved. The alkali going into solution is determined according to **66**. 60

ββ. If a precipitate was produced by sodium hydroxide and redissolved in an excess, add to a portion of this alkaline solution *a little* hydrogen sulphide water (not so much that a considerable excess of the sodium hydroxide does not still remain unchanged). White precipitate: ZINC. Confirm by testing a portion of the original solution with potassium ferricyanide (§ 122, 13). If hydrogen sulphide produced no precipitate, add

* A white precipitate produced by ammonium sulphide, and soluble upon warming with more ammonium sulphide, would be sulphur which had been separated by the action of some body which decomposes ammonium sulphide in alkaline solution (*e.g.*, a ferricyanide which might have been overlooked in 51).

ammonium chloride to the remainder of the alkaline solution, and heat. White precipitate, not soluble in more ammonium chloride: ALUMINIUM. Confirm by testing the filtered and washed precipitate with cobalt solution before the blowpipe (§ 106, 11).

Note to **58** *and* **59**.

Very slight impurities may render indistinct the colors of the precipitates considered in **58** and **59**, and in case this appears to happen, the following method is to be pursued for the detection of manganese, zinc, aluminium, chromium, and silicic acid:

To a part of the original solution add sodium hydroxide solution carefully, first in small amount, then in excess.

aa. *No precipitate is formed:* this indicates **61** SILICIC ACID. Proceed by **60**, *aa*.

bb. *A whitish precipitate is formed*, which does not dissolve in an excess of the precipitant, and quickly becomes brownish-black in the air: MANGANESE. Confirm by fusing with sodium carbonate (§ 123, 14).

cc. *A precipitate is formed* which dissolves in an excess of the sodium hydroxide: CHROMIUM, ALUMINIUM, ZINC.

αα. Add to a portion of the clear alkaline solution a *little* hydrogen sulphide water (not so much that a considerable excess of the sodium hydroxide does not remain unchanged). White precipitate: ZINC. Confirm by precipitating a portion of the original solution with sodium carbonate, and testing the washed precipitate with cobalt nitrate (§ 122, 8 and 15.)

ββ. In case the original solution appears green or violet, or the alkaline solution appears green, and in case the precipitate produced and redissolved by sodium hydroxide

was bluish-green, CHROMIUM (as a chromic salt) is present. Confirm by boiling the alkaline solution or by means of the sodium metaphosphate bead (§ 107, 3 and 11).

γγ. Add ammonium chloride to the alkaline solution, and heat. White precipitate, not soluble when more ammonium chloride is added: ALUMINIUM. Confirm by testing the filtered and washed precipitate with cobalt solution before the blowpipe (§ 106, 11).

4. To a part of the original solution add ammonium chloride and ammonium carbonate, to which some ammonia is added, and warm gently. **62**

a. NO PRECIPITATE IS FORMED: absence of barium, strontium, and calcium. Pass on to **64**.

b. A PRECIPITATE IS FORMED: presence of barium, strontium, or calcium. Filter off the precipitate, wash it, dissolve it in dilute hydrochloric acid, evaporate the solution to dryness, warm the residue with a little water, filter, and add an equal volume of gypsum solution to a portion of the liquid. **63**

α. No turbidity results, even after from 5 *to* 15 *minutes:* CALCIUM. Confirm by boiling a portion of the original solution with a concentrated solution of ammonium sulphate, filtering, and testing the filtrate with ammonium oxalate (§ 102, 3 and 5).

β. No turbidity results at first, but one appears after some time: STRONTIUM. Evaporate a sample of the original solution, after the addition of hydrochloric acid, to dryness, and test by the flame reaction (§ 101, 7 or 8).

γ. A precipitate results at once: BARIUM. Confirm with hydrofluosilicic acid or potassium dichromate (§ 100, 6 and 9).

5. To the portion mentioned at **62**, in which no precipitate has been obtained by ammonium carbonate after the addition of ammonium chloride, add sodium phosphate or ammonium sodium phosphate, then still more ammonia, and with a glass rod gently rub the surface of the glass with which the liquid is in contact. **64**

a. NO PRECIPITATE IS FORMED: absence of magnesium. Pass on to **65**.

b. A CRYSTALLINE PRECIPITATE IS FORMED: MAGNESIUM.

6. Evaporate a small amount of the original solution in a platinum or porcelain dish, and finally ignite gently. If carbonization should occur in consequence of the presence of organic substances, either increase the heat and continue it until the carbon is consumed, or extract the latter with hot water and evaporate the filtrate. **65**

a. NO FIXED RESIDUE REMAINS. Test then for AMMONIUM by adding solid calcium hydroxide to the original solution, observing the odor, the cloud produced with acetic acid, and the reaction of the escaping gas (§ 96, 3).

b. A FIXED RESIDUE REMAINS: potassium or sodium. Add hydrochloroplatinic acid to a small part of the original solution, shake somewhat, and rub with a glass rod. If it reacts alkaline, it is to be first neutralized with hydrochloric acid. If it is dilute, it should be first very much concentrated by evaporation. If it contains organic substances, it is evaporated to dryness, the residue is gently ignited, extracted with water, filtered, the solution is concentrated, and neutralized if necessary with hydrochloric acid. **66**

α. No precipitate, even after 10 *or* 15 *minutes:* SODIUM. Confirm with acid potassium pyroantimonate or by flame coloration (§ 95, 2 and 3).

β. Yellow crystalline precipitate: POTASSIUM. Confirm with sodium acid tartrate or by flame coloration (§ 94, 4 and 6).

Simple Compounds.

A. SUBSTANCES SOLUBLE IN WATER.

I. Detection of One Inorganic Acid.

§ 219.

In the first place consider what acids there are which form soluble compounds with the metal which has been found (compare Appendix IV), and take this

into consideration, as well as the results of the preliminary testing, in making the following examination.

1. ARSENIOUS and ARSENIC ACIDS, as well as SILICIC ACID, **67** have been already detected in the examination for the metals (**52**, **60**).

2. CARBONIC ACID in combination with bases, SULPHUR **68** in the form of metallic sulphides, CHROMIC ACID, and HYDROFERRICYANIC ACID will have been also indicated in the examination for the metals which has been described. The first two are recognized by their effervescence upon the addition of hydrochloric acid. The escaping gases, carbonic acid and hydrogen sulphide, are readily distinguished by the odor of the latter; and, if necessary, the presence of carbonic acid is confirmed by means of lime-water (§ 179, 5), and that of hydrogen sulphide with solution of lead acetate (§ 187, 4). These reagents also permit the detection of free hydrogen sulphide and free carbonic acid in aqueous solution. Chromic acid and hydroferricyanic acid will have been indicated by the separation of sulphur and the changes of color upon the addition of hydrogen sulphide water. Confirm the presence of chromic acid by means of lead or silver solution (§ 166, 8 and 7), and that of hydroferricyanic acid by means of ferrous sulphate (§ 186, *b*).

3. Make a test with the aqueous solution (after sufficiently diluting it with water in case it is concentrated) by acidifying it with hydrochloric acid and adding a little barium chloride, or, if a silver or mercurous salt was found, with nitric acid and barium nitrate. **69**

a. THE LIQUID REMAINS CLEAR: absence of sulphuric acid. Pass on to **70**.

b. A WHITE, FINELY PULVERULENT PRECIPITATE IS OBTAINED: SULPHURIC ACID. This must remain undissolved even when more dilute hydrochloric or nitric acid is added.

4. To a new portion (after it has been made neutral **70** or slightly alkaline with ammonia in case it had an acid reaction, and after filtering if necessary) add some calcium chloride solution diluted with 4 or 5 parts of water.

a. NO PRECIPITATE IS FORMED: absence of phosphoric acid, oxalic acid,* fluorine, and of considerable quantities of boric acid. Pass on to **73.**

b. A PRECIPITATE IS PRODUCED. Add at once an excess of acetic acid. **71**

α. It dissolves easily: PHOSPHORIC ACID OR BORIC ACID. Add ammonium chloride, magnesium sulphate, and ammonia to a portion of the original solution. A crystalline precipitate shows the presence of PHOSPHORIC ACID (§ 172, 7). Test for BORIC ACID according to **76.**

β. It does not dissolve, the liquid appears milk-white after the addition of acetic acid, and the precipitate is pulverulent: OXALIC ACID. Confirm by treating the original substance with manganese dioxide and sulphuric acid (§ 175, 7).

γ. It dissolves with difficulty, usually incompletely, and the undissolved part of the precipitate appears transparent and flocculent: FLUORINE. Test for this by etching glass (§ 176, 5). **72**

5. Acidify a new portion with nitric acid, and then add silver nitrate solution. **73**

a. THE LIQUID REMAINS CLEAR: certain absence of chlorine, bromine, iodine, ferro- and ferricyanogen, as well as of sulphocyanogen; probable absence of cyanogen (in simple cyanides).† Pass on to **76.**

b. A PRECIPITATE IS FORMED.

α. Its color is orange: FERRICYANOGEN. Confirm by testing the original solution with ferrous sulphate (§ 186, *b*). **74**

β. Its color is white or yellowish. Treat the precipitate with ammonia in excess, directly if an alkali

* If a chromic or a ferric salt is present, the fact that a precipitate is not produced does not justify the conclusion that oxalic acid is not present (see § 177). In this case, a portion of the original substance must be tested with concentrated sulphuric acid or with sulphuric acid and manganese dioxide (§ 175, 6 or 7).

† Among the soluble cyanides is mercuric cyanide, which does not give a precipitate with silver nitrate. Whether or not this fact is to be taken into account is seen from the metal which has been found. For a method of detecting cyanogen in this salt, see § 185, 12.

metal or alkali-earth metal is present, but after filtering and washing if an earth metal or a heavy metal is present.

aa. It does not dissolve, even upon warming: IODINE or FERROCYANOGEN. In the first case, the precipitate is pale yellow; in the second case, white and gelatinous. Confirm the presence of iodine with starch and nitrous acid (§ 184, 8), and that of ferrocyanogen by ferric chloride (§ 186, *a*). 75

bb. It dissolves with difficulty in the cold, but more easily upon warming: BROMINE or SULPHOCYANOGEN. The precipitate of silver bromide is yellowish-white, while that of the sulphocyanide is white. Confirm the presence of BROMINE by testing the original solution with chlorine-water (§ 183, 6), and that of SULPHOCYANOGEN with ferric chloride (§ 186, *c*).

cc. It dissolves easily, even in the cold: CHLORINE or CYANOGEN. If cyanogen is present, the original substance usually smells of hydrocyanic acid. Confirm by the addition of a ferrous salt solution, sodium hydroxide, and then hydrochloric acid, to the original solution (§ 185, 6). If cyanogen is not present, the silver precipitate is due to CHLORINE. A sample of the original substance heated with manganese dioxide and sulphuric acid yields chlorine (§ 182, 6).

6. To confirm the presence of BORIC ACID or to detect small quantities of it, add hydrochloric acid carefully to a portion of the aqueous solution until it is just distinctly acid, dip a strip of turmeric-paper half-way in the solution, and dry it at 100°. If the half which has been dipped appears brownish-red, boric acid is present. Confirm by flame coloration (§ 174, 6, 7, 8, or 9). 76

7. Generally the preliminary testing will have already shown the presence of NITRIC and CHLORIC acids (5). Confirm the presence of the first with sulphuric acid and ferrous sulphate (§ 193, 6), and that of the latter by testing the solid salt with concentrated sulphuric acid (§ 194, 7). 77

Simple Compounds.

A. Substances soluble in Water.

II. Detection of One Organic Acid.

§ 220.

In the first place, consider what acids form soluble compounds with the bases that have been found (compare Appendix IV), and take this into consideration, as well as the result of the preliminary testing, in carrying out the following investigation.

It is assumed in the succeeding course that the organic 78
acid is present in the free state or combined with an alkali. If, therefore, there is another base present, it must be first separated. In most cases, this may be done by making the aqueous solution strongly alkaline with sodium carbonate, heating to boiling, and filtering. If the separation by this method presents difficulties, separate the metal, if it belongs to Groups V or VI, by precipitation with hydrogen sulphide after acidifying the liquid with hydrochloric acid; if it belongs to Group IV, with ammonia and ammonium sulphide. After the metallic carbonate or sulphide has been filtered off, and, if necessary, the ammonium sulphide in excess has been removed by acidifying with hydrochloric acid, heating, and filtering off the sulphur, pass on to the following course (79). If the metal belongs to Group III, and cannot be removed by boiling with sodium carbonate (as may be the case if the acid is a non-volatile one), precipitate the latter in a new portion with normal lead acetate, wash the precipitate, suspend it in water, pass in hydrogen sulphide, filter off the lead sulphide, and proceed with the filtrate according to the following course. It is also possible to precipitate alumina from its compounds with non-volatile acids, as aluminium silicate, by means of solution of water-glass. For the separation of acetic acid or formic acid from bases which render their detection difficult, the salts may also be distilled with dilute sulphuric acid, and the acids detected in the distillate.

1. Add hydrochloric acid to a part of the aqueous solution, if it is alkaline, to acid reaction. (If carbonic acid is thereby evolved, remove this by heating and repeated shaking. Excessively long heating is to be avoided, in order not to drive off acetic or formic acid.) To the acid or neutral liquid now add ammonia to alkaline reaction, then ammonium chloride, and not too small an amount of calcium chloride. 79

a. NO PRECIPITATE IS FORMED, NOT EVEN AFTER SHAKING AND AFTER SOME TIME: absence of oxalic acid and tartaric acid. Pass on to **80**.

b. A PRECIPITATE IS PRODUCED.

α. It forms only after some time, and is crystalline: TARTARIC ACID. Confirm by examining the behavior of the washed precipitate with sodium hydroxide solution, or by testing the aqueous solution with potassium acetate and acetic acid (§ 197, 5 and 4).

β. It forms at once and is finely pulverulent: OXALIC ACID. Confirm by testing a new portion of the aqueous solution, acidified with acetic acid, with solution of gypsum (§ 175, 5).

2. Mix the liquid from 1, *a*, with about three volumes of alcohol, close the flask with a stopper, and allow the fluid to stand for several hours. 80

a. It remains clear: no citric, malic, or succinic acid. Pass on to **82**.

b. A white precipitate forms: citric, malic, or succinic acid. Filter it off, suspend it in a little water, add hydrochloric acid drop by drop until the precipitate has just dissolved, then ammonia in excess. Heat the liquid in a flask to gentle boiling, and keep it so for a few minutes.

α. The liquid remains clear: absence of citric acid. Pass on to **81**.

β. A heavy, white precipitate forms: CITRIC ACID. Confirm by preparing the lead salt of the acid, and, after washing it, testing its behavior with ammonia (in which it must be easily soluble), or still better, by the preparation and microscopic examination of

the barium salt, which shows a characteristic crystallization (§ 198, 6 and 5).

3. Make a portion of the original solution, or of the solution prepared according to **78**, *exactly* neutral with ammonia or hydrochloric acid, if it is not already neutral, and add a little ferric chloride solution. If a brownish, pale red precipitate forms, SUCCINIC ACID is present, and if the liquid remains clear, it is MALIC ACID. For further confirmation prepare the lead salt of the acid under examination, and test its properties. (Compare § 199, 5, and § 202, 6.) **81**

4. Make a portion of the original solution *exactly* neutral (if it is not already so) with ammonia or hydrochloric acid, and add first a very small amount of ferric chloride solution, then somewhat more. **82**

a. A FLESH-COLORED, VOLUMINOUS PRECIPITATE IS FORMED: BENZOIC ACID. Confirm by treating the original dry substance with hydrochloric acid (§ 203, 2).

b. AN INTENSE VIOLET COLORATION IS PRODUCED: SALICYLIC ACID.

c. A RATHER INTENSE, DEEP RED COLORATION OF THE LIQUID RESULTS, AND UPON BOILING, A LIGHT BROWNISH-RED PRECIPITATE SEPARATES: acetic acid or formic acid.

Warm a portion of the solid salt under investigation, or of the residue obtained by evaporating the liquid (to which, if it is acid, sodium hydroxide must be previously added until it is neutral) with concentrated sulphuric acid and alcohol (§ 206, 7). An odor of acetic ether allows the recognition of ACETIC ACID.

Confirm the presence of FORMIC ACID, which must be inferred if no acetic acid has been found, by mercuric chloride, and by silver nitrate (§ 207, 6 and 4).

Simple Compounds.

B. SUBSTANCES INSOLUBLE OR DIFFICULTLY SOLUBLE IN WATER, BUT SOLUBLE IN HYDROCHLORIC ACID, NITRIC ACID, OR AQUA REGIA.

*Detection of the Metal.**

§ 221.

I. Dilute a part of the solution in hydrochloric acid, nitric acid, or aqua regia, with water,† and test, in the first place, in case the solution was in nitric acid, by means of the addition of hydrochloric acid, for SILVER, MERCURY (mercurous salt), and large amounts of LEAD (46 to 49). 83

If the solution was effected by hydrochloric acid or aqua regia, ‡ or if a nitric acid solution was not precipitated by hydrochloric acid, mix a portion with an abundant amount of hydrogen sulphide water, and test for the METALS OF THE SECOND DIVISION OF THE FIFTH GROUP, for LEAD, for the METALS OF THE SIXTH GROUP, and for FERRIC SALTS, by 50 to 55.

If a metal of the fifth or sixth groups or a ferric salt is not found, pass on to 84. If a metal is found which has various degrees of oxidation, it is to be borne in mind that in solutions which are prepared by the aid of hydrochloric acid only, the oxides generally go into solution in the condition in which they are present; while upon solu-

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*In this course, some acids in combination alkali-earth metals are taken into consideration, because such salts are encountered.

†If a white turbidity or precipitation is produced by the addition of water, this indicates bismuth or antimony (possibly also tin). (Compare § 141, 9, and § 154, 4.) Warm with hydrochloric acid until the solution has become clear, and then pass on to 50. If the original substance has dissolved with some difficulty in hydrochloric acid, the precipitate resulting upon the addition of water may be lead sulphate, lead chloride, or silver chloride. Test for these according to § 224.

‡If the solution still contains chlorine or nitrosyl chloride, a separation of sulphur is produced upon the addition of hydrogen sulphide, and since this may hide yellow sulphides, the aqua regia solution should be heated before adding hydrogen sulphide until it no longer smells of chlorine. (Compare also the notes in Section III.)

tion in nitric acid or aqua regia, lower degrees of oxidation are usually changed partly or wholly into higher ones. If, therefore, an aqua regia solution is prepared, and a ferric, mercuric, stannic, or arsenic compound is found in it, it requires a special test to determine in which state of oxidation or sulphurization the metals were originally present, so far as the matter has not already been decided by the behavior of the body to the solvent itself. Often (*e.g.*, with mercury salts) treatment with sodium or potassium hydroxide leads at once to a distinction, for they separate yellow mercuric oxide from mercuric salts, and black mercurous oxide from mercurous chloride, etc., while the acids combine with the alkali, and are easily detected in the filtrate.

II. To a portion of the acid solution (which is freed from carbonic acid by heating if necessary, and to which ammonium chloride is added if it contains little free acid) add ammonia to alkaline reaction, and then, without regard to whether ammonia has produced a precipitate or not, add some ammonium sulphide, and warm gently. **84**

a. NO PRECIPITATE IS FORMED, EITHER BY AMMONIA OR AFTER THE ADDITION OF AMMONIUM SULPHIDE: absence of metals of the third * and fourth groups, and also, if not too great an amount of ammonium salts is present, the salts of the alkali-earth metals † to be mentioned in **85**. Make alkaline with ammonia a portion of the acid solution, and proceed, according to **62** to **65**, to test for the alkali-earth and alkali metals.

b. A PRECIPITATE IS PRODUCED.

α. A black one indicates IRON, NICKEL, or COBALT. Distinguish these as in **57**.

β. A *flesh-colored* precipitate: MANGANESE. Confirm according to **58**, *aa*.

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* That this conclusion in regard to aluminium and chromium is uncertain under some circumstances is evident from the second foot-note under **56**.

† If small amounts of these salts are dissolved in much hydrochloric acid, they remain dissolved upon neutralizing the acid with ammonia, on account of the action of the resulting ammonium chloride. In the case of alkali-earth metal borates, this solubility in ammonium salts is rather considerable, so that it may easily happen that somewhat large amounts of these are not precipitated by ammonia.

γ. A *bluish-green* precipitate indicates CHROMIC HYDROXIDE, perhaps also CHROMIC PHOSPHATE.* Confirm in respect to chromium, as in **58**, *bb*. Whether the chromium is combined with phosphoric acid is found by evaporating the original hydrochloric acid solution with nitric acid almost to dryness, and testing with ammonium molybdate (§ 172, 10).

δ. A *white* precipitate: this may be ZINC SULPHIDE. If it was produced by ammonia alone, it may be due not only to ALUMINIUM HYDROXIDE or hydrated SILICIC ACID, but also to a PHOSPHATE, BORATE, OXALATE, SILICATE, or FLUORIDE of an ALKALI-EARTH METAL, or ALUMINIUM PHOSPHATE, since all these are insoluble in water, but soluble in hydrochloric acid, and they therefore separate when the acid is neutralized (since they are but slightly soluble in ammonium chloride). If organic substances are present, a precipitate produced by ammonia may be due to compounds of certain ALKALI-EARTH METALS with TARTARIC or CITRIC ACID. **85**

To determine which of these substances is present proceed as follows:

aa. Recollect whether the preliminary examination has indicated the presence of silicic acid (**20**). If this is the case, evaporate a portion of the hydrochloric acid solution to dryness, moisten the residue with hydrochloric acid, and add water. If silicic acid is present, it remains undissolved. Determine the metal in the solution after **56** or **62**. **86**

bb. Add rather concentrated sodium or potassium hydroxide solution to a portion of the original solution to alkaline reaction; then add more, in order to determine if a resulting precipitate is soluble in an excess, and boil.

αα. *No permanent precipitate is formed.* **87**

Divide the clear alkaline liquid into two parts,

* For the sake of completeness, attention is called to the fact that, under certain circumstances, manganese may be thrown down as green manganese sulphide (compare § 123, 5).

add ammonium chloride to one half, and a little hydrogen sulphide water to the other. A precipitate which is permanent, even after the addition of more ammonium chloride, in the first case shows ALUMINIUM, while a precipitate produced by a small amount of hydrogen sulphide water shows ZINC. Determine whether the aluminium was present as phosphate, as in **84**, *b*, *γ*.

ββ. A permanent precipitate is formed: presence of an alkali-earth metal salt. Now test:

88 1. For PHOSPHORIC ACID and the alkali-earth metal combined with it, by adding ammonia to a portion of the hydrochloric acid solution until a precipitate is formed; then at once acetic acid, drop by drop, until it is just dissolved; and finally add sodium acetate and a drop of ferric chloride solution. If a white, flocculent precipitate is produced, phosphoric acid is present. Now add some more ferric chloride until the liquid has become distinctly red, boil, filter boiling hot, and then, according to **62**, detect in the filtrate, which is now free from phosphoric acid, the alkali-earth metal which had been combined with that acid.

2. For OXALIC ACID, by mixing a portion of the original substance upon a watch-glass with a few drops of water and a little manganese dioxide free from carbonates, and adding a little concentrated sulphuric acid (§ 175, 7). Effervescence shows the presence of oxalic acid. Find the metal by igniting a new portion, dissolving the residue in dilute hydrochloric acid, and testing the solution as in **62** to **65**.

89 3. BORIC ACID is detected in the weak hydrochloric acid solution with turmeric-paper (§ 174, 5); and the metal combined with it, by boiling a portion of the original substance with water and sodium carbonate, filtering, washing, dissolving the resulting carbonate in as little hydrochloric acid as possible, and treating the solution like the one obtained in **63**.

4. Test for FLUORINE by heating the original substance, or the precipitate produced by ammonia in the hydrochloric acid solution, with sulphuric acid (§ 176, 5).

After removing the fluorine, determine which alkali-earth metal, now as sulphate, is in the residue, by treating the latter with hydrochloric acid, testing the solution by **62** for calcium, and eventually for magnesium by **64**. If neither of these is found, examine the residue insoluble in hydrochloric acid for barium and strontium, by § 224.

5. Test for TARTARIC ACID and CITRIC ACID (which can be present only when the substance carbonizes by ignition in a glass tube) and the metals combined with them, by boiling the original substance with a solution of sodium carbonate, and filtering. The alkali-earth metal carbonates are thus obtained upon the filter, while the acids are in the filtrate as sodium salts. Examine the precipitate by **63**, and the solution by **79**.

Simple Compounds.

B. SUBSTANCES INSOLUBLE OR DIFFICULTLY SOLUBLE IN WATER, BUT SOLUBLE IN HYDROCHLORIC ACID, NITRIC ACID, OR AQUA REGIA.

I. Detection of One Inorganic Acid.

§ 222.

1. CHLORIC ACID cannot be present, for all the chlo- **90**
rates are soluble in water. NITRIC ACID, which may be present in the form of a basic salt, must have been already recognized by ignition in the glass tube (**8**, *cc*), and CYANOGEN also (**8**, *gg*). Concerning the CYANOGEN COMPOUNDS insoluble in water, see § 240. The test with the sodium metaphosphate bead, or the solution of the substance, would have called attention to SILICIC ACID. Confirm this by evaporating the hydrochloric acid solution to dryness and treating the residue with hydrochloric acid and water (§ 180, 3).

2. ARSENIOUS and ARSENIC ACIDS,* CARBONIC ACID, CHROMIC **91**
ACID, as well as SULPHUR in the form of sulphides, have

* To distinguish arsenious and arsenic acids in compounds which are insoluble in water but soluble in hydrochloric acid, it is best to use hydrogen sulphide (§ 157, 12).

water) in water and a little ammonia, and testing the neutral solution with ferric chloride (§ 203, 3, and § 204, 3).

4. Boil a sample with an excess of sodium carbonate 97
solution for a long time, and filter hot. In most cases, the organic acids are now in the filtrate as sodium salts. Acidify this filtrate slightly with hydrochloric acid, expel the carbonic acid by warming, and test the liquid as described above in § 220. In the presence of metals of Group IV and of lead, this decomposition is not complete. In such exceptional cases, after boiling with sodium carbonate, add ammonium sulphide to the filtrate until the metal is precipitated, and proceed as given in 78.

Simple Compounds.

C. Substances insoluble or difficultly soluble in Water, Hydrochloric Acid, Nitric Acid, and Aqua Regia.

Detection of the Metal and the Acid.

§ 224.

Under this head, BARIUM SULPHATE, STRONTIUM SUL- 98
PHATE, CALCIUM SULPHATE, CALCIUM FLUORIDE, SILICIC ACID, strongly ignited or native ALUMINA, LEAD SULPHATE, compounds of LEAD with CHLORINE and BROMINE, of SILVER with CHLORINE, BROMINE, IODINE, and CYANOGEN, ignited or native STANNIC OXIDE, ignited CHROMIC OXIDE, and finally SULPHUR and CARBON, are considered as the bodies belonging here which are frequently encountered. In regard to simple silicates refer to § 241, and in respect to ferro- or ferricyanides, to § 240. Whether these are to be taken into consideration is shown by the preliminary tests.

Calcium sulphate and lead chloride are not insoluble in water, while lead sulphate can be dissolved in hydrochloric acid. These compounds, however, are treated here again, since they are so difficultly soluble that a complete solution of them is seldom obtained, so that they may be found here in case they have been overlooked in the examination of the aqueous or acid solution.

1. Free SULPHUR must have been already detected in the preliminary examination (9, *aa*, or 11).

2. CARBON is generally black, insoluble in aqua regia, combustible * upon a platinum foil heated from below by the blowpipe, and it yields potassium carbonate when deflagrated with potassium nitrate.

3. CHROMIC OXIDE is green or blackish-green, and must have indicated its presence already in the test with the sodium metaphosphate bead (18).

4. Cover a small portion of the substance with ammo- 99
nium sulphide.

a. IT BECOMES BLACK: this indicates the presence of a lead or silver salt.

α. It fused in the tube without decomposition (3): lead chloride or bromide, silver chloride, bromide, or iodide. Fuse 1 part of the compound with 4 parts of sodium-potassium carbonate in a small porcelain crucible, allow the mass to cool, boil it with water, and test the filtrate for CHLORINE, BROMINE, and IODINE by 73; dissolve the residue, which is either METALLIC SILVER or LEAD OXIDE in nitric acid, and test the solution according to 46.

β. It evolved cyanogen and left metallic silver when ignited in the glass tube: SILVER CYANIDE.

γ. It remained unchanged when ignited in the glass tube: LEAD SULPHATE. Boil a sample with sodium carbonate solution, filter, acidify the filtrate with hydrochloric acid, and test it with barium chloride for SULPHURIC ACID. Dissolve the washed residue in nitric acid, and test the solution with hydrogen sulphide and with sulphuric acid for LEAD (§ 137, 4 and 8).

b. IT REMAINS WHITE: absence of a lead or silver 100
salt.

α. Test a portion for stannic oxide by means of a borax bead colored faintly bluish with copper oxide, in the reducing flame (§ 152, 15). If a reddish-brown to ruby-red coloration appears, confirm the presence of stannic oxide by the reduction of

* Graphite is completely consumed only by strong ignition in a stream of oxygen.

a portion with sodium carbonate and potassium cyanide or with sodium formate (§ 152, 14).

β. Mix a small portion intimately with *finely ground* quartz-powder, moisten the mixture in a crucible with a few drops of concentrated sulphuric acid, and warm gently upon an iron plate or a small sand-bath. (Direct heating over the lamp easily leads to incorrect conclusions.)

aa. White vapors are evolved which redden litmus, and cause a drop of aqueous ammonia held above it to become turbid: CALCIUM FLORIDE is indicated. Decompose a finely pulverized portion with sulphuric acid in a platinum crucible, and confirm the presence of fluorine by etching glass (§ 176, 5). Boil the residue with hydrochloric acid, filter and detect the CALCIUM, after neutralizing with ammonia, by means of ammonium oxalate.

bb. No vapors are evolved which redden litmus or make a drop of aqueous ammonia turbid. Mix a small portion of the finely pulverized substance with 4 parts of pure sodium-potassium carbonate, and fuse in a platinum crucible (or upon platinum foil). Boil the mass with water, filter, if a residue remains, and wash it. Then test a portion of the filtrate, after acidifying it with hydrochloric acid, with barium chloride, for SULPHURIC ACID, and in case this is not found, another portion for SILICIC ACID by evaporating the liquid acidified with hydrochloric acid (§ 180, 2). If this also is absent, test the hydrochloric acid solution of the residue left upon evaporation, with ammonia for ALUMINIUM.

If PURE SILICIC ACID was present, the mass obtained by fusion with sodium-potassium carbonate must have dissolved clear in water; but if there were silicates present, the bases of these remained undissolved, and may be examined further (see § 241). When ALUMINA is present, complete solution of the fused mass in water can

be expected only when a large amount of alkali carbonate has been used, and a high temperature has been employed.

If sulphuric acid was found, the metal which was combined with it remains upon the filter as carbonate. Dissolve it, after complete washing, in dilute hydrochloric acid, evaporate to dryness, treat the residue with water, and test for BARIUM, STRONTIUM, and CALCIUM by **63**.

*Complex Compounds.**

A. SUBSTANCES SOLUBLE AND INSOLUBLE IN WATER, BUT SOLUBLE IN HYDROCHLORIC ACID, NITRIC ACID, OR AQUA REGIA.

Detection of the Metals.†

§ 225.‡

Treatment with Hydrochloric Acid: Detection of Silver, Mercury in Mercurous Compounds (Lead).

The systematic method for detecting the metals is essentially the same, whether the substance is soluble in water or whether it is soluble only in acids. Where a special procedure is necessary in consequence of the varying nature of the original solution, this will be distinctly specified. **101**

I. THE SOLUTION IS SIMPLY IN WATER.

MIX THE PORTION INTENDED FOR THE DETECTION OF THE METALS WITH SOME HYDROCHLORIC ACID. **102**

1. THE SOLUTION HAD AN ACID OR NEUTRAL REACTION PREVIOUSLY TO THE ADDITION OF THE HYDROCHLORIC ACID.

a. NO PRECIPITATE IS FORMED: this indicates the absence of silver and (mercurous) mercury. Pass on to § 226.

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* This expression is used here and subsequently for compounds in which all the commonly occurring basic and acid radicals may be present.

† Compare the notes in Section III, with which the operator should become familiar FIRST OF ALL. In this course, consideration is taken of the acids of arsenic, as well as of those salts of the metals of Groups II and III, which dissolve in hydrochloric acid, and are precipitated unchanged by neutralizing the acid with ammonia.

‡ Compare the notes in Section III.

b. A PRECIPITATE IS FORMED. Add more hydrochloric acid, drop by drop, until the precipitate ceases to increase; then add about 6 or 8 drops more of the acid, stir the mixture, and filter.

The precipitate produced at first by hydrochloric acid may consist of silver chloride, mercurous chloride, lead chloride, a basic salt of antimony, bismuth oxychloride, metastannic chloride, possibly also, if the preliminary examination showed the presence of organic substances, benzoic acid and salicylic acid. The basic salt of antimony and the bismuth oxychloride, however, redissolve in the excess of hydrochloric acid; consequently, if the instructions given have been strictly followed, the precipitate collected upon the filter can consist only of silver chloride, mercurous chloride, and lead chloride (possibly also of the very rare metastannic chloride and benzoic and salicylic acids, which, however, are disregarded here).

Wash the precipitate collected upon the filter 103
twice with cold water, add the washings to the filtrate, and examine the solution as directed in § 226, even though the addition of the washings to the acid filtrate should produce turbidity in the fluid (which indicates the presence of antimony or bismuth, or possibly also of lead chloride or metastannic chloride).

Treat the twice-washed precipitate on the filter as follows:

α. Pour hot water over it upon the filter, and test the fluid running off with hydrogen sulphide and with sulphuric acid for LEAD. (The non-formation of a precipitate simply proves that the precipitate produced by hydrochloric acid contains no lead, and does not by any means establish the total absence of this metal, as hydrochloric acid fails to precipitate lead from dilute solutions.) If the hydrochloric acid precipitate contains lead chloride, wash it several times with hot water to dissolve out the lead salt.

β. If there is a residue remaining on the filter, pour ammonia upon it. If this changes its color

to black or gray, it is a proof of the presence of a MERCUROUS SALT.

γ. Add to the ammoniacal fluid running off in *β*, nitric acid to strongly acid reaction. The formation of a white, curdy precipitate, or, with minute quantities, an opalescence of the liquid, indicates the presence of SILVER.*

2. THE ORIGINAL AQUEOUS SOLUTION HAD AN ALKALINE REACTION. 104

a. THE ADDITION OF HYDROCHLORIC ACID TO STRONGLY ACID REACTION FAILS TO PRODUCE EVOLUTION OF GAS OR A PRECIPITATE, OR THE PRECIPITATE WHICH FORMS AT FIRST REDISSOLVES UPON FURTHER ADDITION OF HYDROCHLORIC ACID. Pass on to § 226.

b. THE ADDITION OF HYDROCHLORIC ACID PRODUCES A PRECIPITATE WHICH DOES NOT REDISSOLVE IN AN EXCESS OF THE PRECIPITANT, EVEN UPON BOILING.

α. *The formation of the precipitate is attended neither with evolution of hydrogen sulphide nor of hydrocyanic acid.* 105 Filter, and treat the filtrate together with the wash-water as directed in § 226.

aa. THE PRECIPITATE IS WHITE. It may, in that case, consist of a salt of lead or silver, insoluble or difficultly soluble in water and hydrochloric acid (LEAD CHLORIDE, LEAD SULPHATE, SILVER CHLORIDE, etc.), or it may be SILICIC ACID (also, if the preliminary tests showed an organic substance, benzoic or salicylic acid, which, however, will not be tested for here). Test it for the bases and acids of these compounds as directed in § 239, bearing in mind that the lead chloride or silver chloride which may be found may possibly have been formed in the process.

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* If benzoic and salicylic acids may be present, according to the preliminary examination, dilute the liquid containing the suspended precipitate with water, and heat to boiling, in order to avoid confusing silver chloride (which will then remain undissolved) with the acids under consideration. In case there was still lead chloride in the precipitate, the ammoniacal solution usually appears turbid, from the separation of a basic lead salt. This has no effect upon the test for silver, since the basic lead salt dissolves upon the addition of nitric acid.

bb. THE PRECIPITATE IS YELLOW OR ORANGE. In that case, it may consist of ARSENIOUS SULPHIDE, and if the liquid from which it has separated was not boiled long, or only with very dilute hydrochloric acid, also of ANTIMONY SULPHIDE or STANNIC SULPHIDE, which substances were originally dissolved in ammonia, caustic potash or soda, sodium phosphate, or some other alkaline fluid, with the exception of alkali sulphides and cyanides. Examine the precipitate, which may also contain SILICIC ACID, as directed in **40**.

*β. The formation of the precipitate is attended with evolution of hydrogen sulphide, but not of hydrocyanic acid.**

aa. THE PRECIPITATE IS OF A PURE WHITE COLOR **106** (dissolving completely upon thoroughly shaking a portion with benzol or petroleum-ether), AND CONSISTS OF SEPARATED SULPHUR. In that case, a POLYSULPHIDE of an ALKALI METAL is generally present. The presence of such a body may be detected also by the yellow or brownish-yellow color of the alkaline solution, and the odor of hydrogen persulphide which accompanies that of hydrogen sulphide on the addition of an acid. Boil, filter, and treat the filtrate as directed in § 230, and the precipitate as directed in § 239.

bb. THE PRECIPITATE IS COLORED (or was not completely soluble in benzol or petroleum-ether). In that case, it may be concluded that a SULPHUR SALT is present, *i.e.*, a compound consisting of an alkali-metal sulphide with the sulphide of a more electro-negative metal or element. The precipitate may accordingly consist of GOLD SULPHIDE, PLATINUM SULPHIDE, STANNIC SULPHIDE, or a SULPHIDE of ARSENIC or ANTIMONY. It might, however, consist also of MERCURIC SULPHIDE or of CUPRIC SULPHIDE or NICKEL SULPHIDE, or contain these

* Should the odor of the evolved gas leave any doubt regarding the actual presence or absence of hydrocyanic acid, add some potassium chromate to a portion of the liquid, previously to the addition of the hydrochloric acid.

substances, as the first dissolves readily in potassium sulphide and in small quantities in ammonium sulphide, and the last two are slightly soluble in ammonium sulphide. Filter and treat the filtrate according to § 230, and the precipitate as directed in **40**.

γ. The formation of the precipitate is attended with evolution of hydrocyanic acid, with or without simultaneous disengagement of hydrogen sulphide: this indicates the presence of an ALKALI-METAL CYANIDE, and if the evolution of hydrocyanic acid is attended with that of hydrogen sulphide, also of an ALKALI-METAL SULPHIDE. In this case, the precipitate may contain, besides the compounds enumerated in *α* and *β*, many other substances (*e.g.*, nickel cyanide, silver cyanide, etc.). Boil, with further addition of hydrochloric acid or even of nitric acid, until the whole of the hydrocyanic acid is expelled, and treat the solution, or (if any undissolved residue has been left) the filtrate, as directed in § 226; and the residue (if any) according to § 239 or § 240. **107**

c. THE ADDITION OF HYDROCHLORIC ACID FAILS TO PRODUCE A PERMANENT PRECIPITATE, BUT CAUSES EVOLUTION OF GAS. **108**

α. The escaping gas smells of hydrogen sulphide: this indicates a SIMPLE ALKALI-METAL SULPHIDE, or a HYDROSULPHIDE of an ALKALI or ALKALI-EARTH METAL. Proceed as directed in § 230.

β. The escaping gas has the scarcely noticeable odor of carbonic acid: in this case, it is CARBON DIOXIDE which was combined with an alkali. Pass on to § 226.

γ. The escaping gas smells of hydrocyanic acid (not considering whether hydrogen sulphide or carbonic acid is evolved at the same time): this indicates an ALKALI-METAL CYANIDE. Boil until the whole of the hydrocyanic acid is expelled, then pass on to § 226.

II. THE SOLUTION IS IN HYDROCHLORIC ACID OR IN NITRO-HYDROCHLORIC ACID.

Proceed as directed in § 226.

III. THE SOLUTION IS IN NITRIC ACID.

Dilute a small portion with water, and should this pro- **109**
duce turbidity or a precipitate (indicative of bismuth), add nitric acid until the fluid is clear again, then hydrochloric acid.

1. NO PRECIPITATE IS FORMED: absence of silver and (mercurous) mercury. Treat the principal solution as directed in § 226.

2. A PRECIPITATE IS FORMED. Treat a larger portion of the nitric acid solution in the same way, filter, and examine the precipitate as directed in **103**, and the filtrate according to § 226.

§ 226.*

Treatment with Hydrogen Sulphide: † *Precipitation of the Metals of Group V, 2d Division, and of Group VI.*

ADD TO A *small portion* OF THE CLEAR ACID SOLUTION HYDROGEN SULPHIDE WATER, UNTIL THE ODOR IS DISTINCTLY PERCEPTIBLE AFTER SHAKING THE MIXTURE, AND WARM GENTLY.

1. NO PRECIPITATE IS FORMED, even after the lapse of some **110**
time. Pass on to § 230, for lead, bismuth, cadmium, copper, mercury, gold, platinum, antimony, tin, and arsenic ‡ are not present.§ The absence of (ferric) iron, of chromates,

* Compare the remarks in Section III concerning this.

† In relation to other courses of analysis in which hydrogen sulphide is avoided, being replaced by ammonium or sodium thiosulphate, by ammonium thiocarbonate or thioacetate, or also by oxalic acid, compare C. HIMLY, Ann. d. Chem. u. Pharm., **43**, 150; H. VOHL, *ibid.*, **96**, 237; A. ORLOWSKI, Zeitschr. f. analyt. Chem., **22**, 357; H. HAGER, Pharmac. Centralhalle., 1885, p. 368; R. SCHIFF and N. TARUGI Ber. d. deutsch. chem. Gesellsch., **27**, 3437; C. LUCKOW, Zeitschr. f. analyt. Chem., **26**, 9.

‡ To obtain conclusive evidence of the absence of arsenic acid, allow the fluid to stand for some time at a gentle heat (about 70°), or heat it with sulphurous acid before adding the hydrogen sulphide (compare § 156, 3). The preliminary examination generally shows the need of this.

§ In solutions containing much free acid, the precipitates are frequently formed only after the addition of a relatively large amount of hydrogen sulphide water.

and of hydroferricyanic acid, is also indicated by this negative reaction.

2. A PRECIPITATE IS FORMED.

a. The precipitate is of a pure white color, light, and finely pulverulent, and does not redissolve on addition of hydrochloric acid. It consists of separated sulphur, and indicates the presence of IRON as a FERRIC SALT. * In order to be sure of the fact that the sulphur is not mixed with a small quantity of yellow sulphides, the color of which is hidden by the greater amount of sulphur, add to the cooled liquid about 2 cc of benzol or petroleum-ether, and shake repeatedly and thoroughly. If no separation of a colored substance appears in the layer of benzol or petroleum-ether, the white precipitate consisted simply of sulphur, and none of the other metals enumerated in 110 can be present. Treat the principal solution as directed in § 230. But if the layer of benzol or petroleum-ether contained a colored precipitate, proceed according to 112. 111

If a separation of sulphur, the original color of the solution, and the change of color by the action of hydrogen sulphide have shown the presence of chromic acid, this is first reduced to a chromic salt by the addition of aqueous sulphurous acid, or, if a precipitate is produced by the latter, by heating with hydrochloric acid and a little alcohol. (Compare § 166, 5.)

b. The precipitate is colored.

To the principal portion of the acid or acidified solution (best in a small flask) add hydrogen sulphide water in excess, *i.e.*, until the fluid smells distinctly of it after shaking, and the precipitate ceases to in- 112

* Sulphur will also precipitate if sulphurous acid, iodic acid, bromic acid, or nitrous acid is present (which substances are not included in this analytical course), and also if chromic acid, or chloric acid, or free chlorine, or also, upon continued heating, if hydroferricyanic acid is present. In presence of chromic acid the reddish-yellow color of the solution changes to green, and in the presence of hydroferricyanic acid the liquid usually assumes a blue color, so that the sulphur suspended in it has the appearance of a bluish precipitate.

crease upon further addition of the reagent; apply a gentle heat, shake vigorously for some time, filter, keep the filtrate (which contains the metals present of Groups I–IV) for further examination according to § 230, and *thoroughly* wash (see § 7) the precipitate, which contains the sulphides of the metals present of Groups V and VI.*

In many cases, and more particularly where there is any reason to suspect the presence of arsenic, it will be found more convenient to transmit hydrogen sulphide gas through the solution DILUTED WITH WATER, instead of adding hydrogen sulphide water. When arsenic acid is suspected, keep the liquid at about 70° during the transmission of the gas.

If the precipitate is yellow,† it consists princi- 113
pally of arsenious sulphide, stannic sulphide, or cadmium sulphide; if orange-colored,† this indicates antimony sulphide; if brown or black, one at least of the following metals must be present: lead, bismuth, copper, mercury as a mercuric salt, gold, platinum, or tin as a stannous salt. However, as a yellow precipitate may contain a small portion of an orange-colored, a brown, or even a black precipitate, without causing its color to be very perceptibly altered thereby, it will always prove the safest way to assume the presence of all the metals named in **110** in any colored precipitate produced by hydrogen sulphide, and to proceed, therefore, as the next paragraph directs.

* The precipitate obtained by hydrogen sulphide from an acid solution may also contain zinc and iron, in exceptional cases, *e.g.*, zinc if alkali-metal acetates were present, and iron if the solution contained stannic chloride with but little free acid (L. STORCH).

† Solutions containing several metals sometimes give with hydrogen sulphide, precipitates whose color does not correspond to that which would be expected from that of the single sulphides, *e.g.*, a solution of mercuric chloride mixed with stannic chloride may give, even with an excess of hydrogen sulphide, a fine yellow or orange-red precipitate, a fact that should be considered.

§ 227.*

Treatment of the Precipitate produced by Hydrogen Sulphide with Ammonium Sulphide: Separation of the 2d Division of Group V from Group VI.

INTRODUCE INTO A TEST-TUBE† A SMALL PORTION OF THE THOROUGHLY WASHED PRECIPITATE PRODUCED BY HYDROGEN SULPHIDE IN THE ACIDIFIED SOLUTION, ADD A LITTLE WATER, AND FROM TEN TO TWENTY DROPS OF LIGHT YELLOW (BUT NOT DARK YELLOW) AMMONIUM SULPHIDE, OR (IF THE CASE REQUIRES IT) SODIUM SULPHIDE,‡ AND EXPOSE THE MIXTURE FOR A SHORT TIME TO A GENTLE HEAT. 114

1. THE PRECIPITATE DISSOLVES COMPLETELY IN AMMONIUM (OR SODIUM) SULPHIDE: absence of the metals of Group V (cadmium, lead, bismuth, copper, mercury.) Treat the remainder of the precipitate (of which a portion has been digested with ammonium sulphide) as directed in § 228. (If the precipitate produced by hydrogen sulphide was so trifling that the whole of it has been used in treating with ammonium sulphide, precipitate the solution ob- 115

* Compare the remarks in Section III.

† If there is a somewhat large precipitate, this may be readily effected by means of a small spatula of platinum, glass, or horn; but if there is only a very trifling precipitate, spread out the filter in a porcelain dish, and treat the whole of it with ammonium sulphide, or, if the case requires it, sodium sulphide.

‡ If copper is present in the solution (a circumstance which is usually indicated by its color, but which is to be determined with certainty by a preliminary test with a bright iron wire, see § 140, 12), then, instead of ammonium sulphide (in which copper sulphide is not quite insoluble, see § 140, 5), yellowish sodium sulphide solution is used, and the precipitate is heated with it just to boiling. If, however, a liquid contains a mercuric salt in addition to copper (and the presence of a mercuric salt is almost always revealed by the various changes in the color of the precipitate occurring upon the addition of hydrogen sulphide water (§ 139, 3), while in case of uncertainty it may be detected by a preliminary test of the original solution with stannous chloride after acidifying with hydrochloric acid), then ammonium sulphide must be used, although the separation of the sulphides of the sixth group from copper sulphide is not quite complete, because mercuric sulphide would dissolve in sodium sulphide and would impede the further examination of the sulphides of the sixth group. But even when these precautions are heeded, it is not always possible to prevent copper going into solution, because some copper sulphide dissolves in sulphur salts, *e.g.*, those of the sulphides of arsenic and tin, even when these contain sodium sulphide as the sulphur base.

tained in that process by addition of hydrochloric acid, filter, wash the precipitate, and treat it as directed in § 228.)

2. THE PRECIPITATE IS NOT DISSOLVED, OR AT LEAST NOT COMPLETELY, even on heating with more yellowish ammonium sulphide (or sodium sulphide): presence of metals of Group V. Dilute with 4 or 5 parts of water, or, if the case requires it, with a 10 per cent solution of ammonium nitrate,* filter the liquid, and mix the filtrate with hydrochloric acid in slight excess. (If it was necessary to treat the whole amount of the hydrogen sulphide precipitate with ammonium sulphide, then mix only a part of the solution with hydrochloric acid.) 116

a. NOTHING BUT A PURE WHITE TURBIDITY IS OCCASIONED, which gives no colored precipitate upon shaking the liquid with benzol or petroleum-ether (compare 111). In this case, the precipitate is PURE SULPHUR: absence of the metals of Group VI (gold, platinum, tin, antimony, and arsenic). Treat the rest of the precipitate (of which a portion has been digested with ammonium sulphide), or, where the case requires it, the whole precipitate treated with ammonium sulphide and washed, according to § 229.

b. A colored precipitate is formed, or a colored precipitate remains in the layer of benzol or petroleum-ether: presence of metals of Group VI with those of Group V. Treat the entire precipitate produced by hydrogen sulphide as the portion has been treated, *i.e.*, digest it with yellow ammonium sulphide (or sodium sulphide), let it subside, pour the supernatant liquid (which must show a yellowish color) on a filter, digest the residue in the flask once more with yellow ammonium sulphide (or sodium sulphide), and filter.† 117

* If the solution from which the precipitation with hydrogen sulphide was made contained a mercuric salt together with a stannic salt, the mercuric sulphide goes into the ammonium sulphide solution more or less completely upon diluting with water, and this is prevented by the addition of ammonium nitrate (TH. WILM. R. CUSHMAN). A part of the tin remains with the sulphides of Group V, and is found according to § 229.

† If the residue remaining upon treatment with ammonium or sodium sulphide does not subside readily, so that the liquid cannot be poured off, trans-

Dilute with water the filtrate (or the remainder of the filtrate when it was necessary to treat the whole of the hydrogen sulphide precipitate with ammonium sulphide) containing the metals of Group VI as sulphur salts, add hydrochloric acid to distinct acid reaction, warm gently, filter the resulting precipitate containing the sulphides of Group VI mixed with sulphur, wash the precipitate completely, and proceed with it according to § 228. Wash the residue left by treatment with ammonium or sodium sulphide (containing the sulphides of Group V) with water in ordinary cases, but in presence of mercury with a 10 per cent solution of ammonium nitrate (see the foot-note under 116), and proceed with it according to § 229.

§ 228.*

Detection of the Metals of Group VI: Arsenic, Antimony, Tin, Gold, Platinum.

118 If the precipitate consisting of the sulphides of Group VI has a PURE YELLOW COLOR, this indicates principally arsenic and (stannic) tin; if it is distinctly ORANGE-YELLOW, antimony is sure to be present; if it is BROWN or BLACK, this denotes the presence of (stannous) tin, platinum, or gold.

Beyond these general indications, the color of the precipitate affords no safe guidance. It is therefore always advisable to test a yellow precipitate, also, for antimony, gold, and platinum, since minute quantities of the sulphides of these metals are completely hidden by a large quantity of stannic sulphide or sulphide of arsenic. In many cases, however, it is possible to conclude, from a general consideration of the substance under examination, that gold and platinum are absent, and since the course

fer the whole to a filter, and when the liquid has run off, spread out the paper, together with the residue, in a porcelain dish, and treat it there as above. If the suspended sulphides are so finely divided that the liquid cannot be filtered clear, add some ammonium nitrate, let it stand for a considerable time at a gentle heat, and then filter.

* Consult the notes in Section III.

of investigation is more complicated in their presence, the case where the presence of gold and platinum may be disregarded is distinguished below from that in which such an assumption is not justified.

1. THERE IS REASON FOR DISREGARDING THE PRESENCE OF GOLD AND PLATINUM.

Heat a little of the precipitate upon the cover of a porcelain crucible or upon a piece of glass or porcelain.* 119

a. NO FIXED RESIDUE IS LEFT: probable presence of ARSENIC; absence of the other metals of Group VI. Confirm by warming a portion of the precipitate with a small amount of concentrated nitric acid, diluting, and testing the filtered liquid with ammonium molybdate for arsenic acid (§ 156, 9), or by digesting a portion with ammonia, filtering, evaporating the filtrate with a fragment of sodium carbonate, and fusing the residue with potassium cyanide and sodium carbonate in a current of carbon dioxide (§ 155, 13). Whether the arsenic was present as arsenious or arsenic acid is determined by the methods given in § 157, 12.

b. A FIXED RESIDUE REMAINS. In this case, consideration is to be taken of tin, antimony, and arsenic.† Dry the remainder of the precipitate completely on the filter, triturate it with about 1 part of dry sodium carbonate and 1 part of sodium (not potassium) nitrate, and transfer the mixture in small portions at a time to a porcelain crucible, in which 2 parts of sodium nitrate have previously been brought just to fusion by moderate heating.‡ As soon as complete oxidation is effected, 120

* It is self evident that this preliminary test may be omitted if the precipitate has any other than a yellow color, and that a decisive result can be obtained only when the precipitate submitted to the test has been completely washed.

† This method (given in *b*) is especially adapted for the detection of tin, antimony, and arsenic, when both tin and arsenic are present in rather large quantity. If the precipitate contains only very small quantities of these metals, the method described in § 157, 2, is to be preferred.

‡ Unnecessarily strong heating of the fusion is to be avoided throughout the operation. If amount of the precipitate is so minute that the

pour the mass upon a piece of porcelain or the cover of a porcelain crucible. After cooling, soak the fused mass* (the portion still adhering to the inside of the crucible as well as the portion poured out on the porcelain) in cold water, filter from the insoluble residue (which must remain if the mass contained antimony or tin) through a moistened filter, and wash thoroughly with a mixture of about equal parts of water and alcohol. (The alcohol is added to prevent the solution of the acid sodium pyroantimonate. The washings are not added to the filtrate.) The filtrate and the residue are now examined as follows:

α. EXAMINATION OF THE FILTRATE FOR ARSENIC 121 (which must be present in the form of sodium arsenate). Add nitric acid to the fluid to distinct acid reaction,† heat to expel carbonic and nitrous acids, add a small portion of the solution to 2 or 3 cc of the solution of ammonium molybdate in nitric acid (§ 55), and heat to brisk boiling. If there is then produced no yellow, or at least no yellowish, precipitate (a pure white one would have no significance), arsenic is not present, but if such a precipitate is formed the presence of arsenic is shown (§ 156, 9).

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operation described cannot be conveniently performed, cut the filter, with the dried precipitate adhering to it, into small pieces, triturate these with some sodium carbonate and nitrate, and project both the powder and the paper into the fusing sodium nitrate. It is *preferable*, however, in such cases, to procure, if practicable, a larger amount of the precipitate, as otherwise there will be little hope of effecting the positive detection of all the metals present.

* Supposing all the metallic sulphides of the sixth group to have been present, the fused mass would consist of sodium antimonate and arsenate, stannic oxide, sodium sulphate, carbonate, nitrate, and some nitrite. With too strong heating, sodium stannate is also formed (compare § 157, 1). (If the precipitate contained gold and tin at the same time, the fusion often appears light red.)

† Upon acidifying the solution with nitric acid, if too high a heat has been used in making the fusion, a small precipitate (of stannic hydroxide) may separate. This should be filtered off, and tested like the undissolved residue. In connection with this, it is to be considered that this precipitate may contain arsenic. Small amounts of arsenic may consequently be overlooked when fusions containing tin are too strongly heated.

For further confirmation, divide the main part of the remaining liquid into two portions. Add to the one part not too little silver nitrate, filter in case silver chloride* should have separated, pour upon the filtrate, down along the side of the tube held slanting, a layer of dilute ammonia (1 part of ordinary ammonia to 2 parts of water, or better still 2 parts of alcohol), and allow this to stand some time without shaking. The formation of a reddish-brown precipitate, which appears as a cloud between the two layers (seen most readily by reflected light), denotes the presence of ARSENIC. If the arsenic is present in some quantity, and the free nitric acid of the solution is exactly neutralized with ammonia, the fluid being stirred during this process, the precipitate of silver arsenate which forms imparts a brownish-red color to the entire liquid.

Add to the other portion of the acidified solu 122
tion, first ammonia, then a mixture of magnesium sulphate and ammonium chloride, and rub the interior walls of the vessel gently with a glass rod. A crystalline precipitate of ammonium magnesium arsenate, which often forms only after long standing, and is deposited more particularly on the sides of the vessel, shows the presence of arsenic. By way of further confirmation, the precipitate may be washed with water containing ammonia, dissolved in dilute hydrochloric acid, and the solution precipitated by hydrogen sulphide, with the aid of a gentle heat; or the arsenic may be reduced to the metallic state (compare § 155 and § 156.) Whether the arsenic was present in the arsenious or arsenic form may be ascertained by the methods described in § 157, 12.

β. EXAMINATION OF THE RESIDUE FOR ANTIMONY AND 123
TIN. As the antimony, if present in the residue, must exist as white, pulverulent, acid sodium pyro-

* Silver chloride will separate if the reagents were not entirely pure, or if the precipitate of sulphides was not completely washed.

antimonate, and the tin as white, flocculent stannic oxide, the appearance of the residue is in itself sometimes indicative of its nature. But it must be noted that on account of the slight solubility of copper sulphide in ammonium sulphide, sodium thioarsenate or sodium thiostannate, a little cupric oxide may also be present in this residue. Transfer the precipitate to the lid of a platinum crucible, or to a small platinum dish, heat it with hydrochloric acid, add a little water, and, whether the precipitate has completely dissolved or not, put in a small, compact lump of pure zinc (as free as possible from lead). The tin and antimony are now changed to the metallic state by the action of the zinc. The ANTIMONY reveals its presence at once, or after a short time, by blackening the platinum. As soon as the disengagement of hydrogen has nearly stopped, take out the remainder of the zinc,* remove the solution of zinc chloride by careful decantation and washing with water; warm the metals for a short time with hydrochloric acid, and test a part of the solution (which, if TIN is present, must contain stannous chloride) by means of mercuric chloride * (§ 152, 9). The separated antimony (and also any copper present) remains almost completely undissolved in the operation of warming with hydrochloric acid, and, after dissolving it with hot nitric acid containing a little tartaric acid, it may be tested further with hydrogen sulphide. If the solution contains copper, precipitate this as cuprous sulphocyanide (§ 140, 10) before testing with hydrogen sulphide.†

The state of oxidation in which any tin or anti-

* Small quantities of tin may have been deposited firmly upon the zinc. This tin may be found by dissolving the zinc in hydrochloric acid, and testing the filtered solution with mercuric chloride (§ 152, 9).

† If there is still doubt about the presence of antimony, for small amounts of it separated upon platinum dissolve upon warming with hydrochloric acid (§ 154, 9), test the remainder of the hydrochloric acid solution with tin upon a platinum surface, according to § 157, 1.

mony found was originally present is determined according to § 157, 10 or 11.

2. THE PRESENCE OF GOLD AND PLATINUM CANNOT BE DISREGARDED. 124

In this case, use is made of the fact that the sulphides of tin, antimony, and arsenic, are volatilized as chlorine compounds when they are heated with an intimate, dry mixture of 3 to 5 parts of ammonium chloride and 1 part of ammonium nitrate, while the sulphides of gold and platinum, under this treatment, are decomposed, and the metals are left behind.

The operation is conveniently carried out in the apparatus shown in Fig. 45.

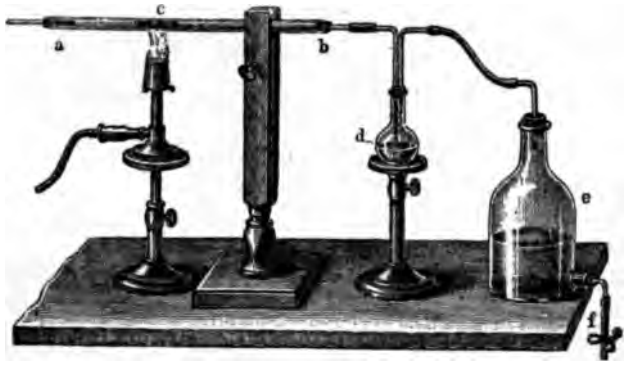

FIG. 45.

The tube *ab* should be 30 to 40 cm long and about 16 mm in diameter. The porcelain boat *c*, intended to receive the mixture, is similar to the one shown in Fig. 41 (p. 290), but should be generally somewhat longer (7 cm long). The flask *d*, of about 150 to 180 cc capacity, is half filled with water containing a little hydrochloric acid. The bottle *e*, serving as an aspirator, should hold about 2 liters.

After the apparatus is set up, mix the *dry* precipitate of, or containing, the sulphides of the sixth group with about 6 parts of the intimate mixture of ammonium chloride and nitrate, by careful trituration together, place the mixture in the boat, introduce this into the tube *ab* at the place indicated in the figure, put in at *a* the stopper provided

with a short, open glass tube, open the cock *f* (glass stop-cock or screw pinch-cock), and thus produce a moderate current of air from *a* towards *b*. Then heat the contents of the boat, gently at first, then more strongly, and finally intensely. There is soon formed near *c* (between *c* and *b*) a white, gradually increasing sublimate.

As soon as all volatile matter has been expelled from the boat, allow it to cool, and draw it out of the tube by means of a wire provided with a hook. If nothing is left behind in the boat, then gold and platinum are not present. If a residue with a metallic aspect is found in it, the first part of the operation is finished; but if the residue presents an appearance which leads to the conclusion that all the antimony, tin, and arsenic are not yet volatilized, some more of the mixture of ammonium chloride and nitrate is put upon it, it is again put into the tube, and heated as before. The residue and the sublimate are now tested in the following manner:

a. RESIDUE. Dissolve it in aqua regia, evaporate the solution to a small volume, and test it by § 151 for GOLD and PLATINUM.

b. SUBLIMATE. Rinse the tube *ab* with the aid of the acid water placed in front in the flask *d* (which sometimes appears whitish from a turbidity), precipitate with hydrogen sulphide, disregarding any turbidity in the solution; filter, wash the precipitate, dry it, and then treat it according to **119** to **124**, to test it for TIN, ANTIMONY, and ARSENIC.*

§ 229.†

Detection of the Metals of Group V, 2d Division: Lead, Bismuth, Copper, Cadmium, Mercury (in Mercuric Salts).

THOROUGHLY WASH THE PRECIPITATE WHICH HAS NOT **125** BEEN DISSOLVED BY AMMONIUM SULPHIDE (OR SODIUM SULPHIDE), AND BOIL WITH DILUTE NITRIC ACID. This operation is performed best in a small porcelain dish in such a manner that the precipitate is heated with a little water,

* In regard to another method for separating gold and platinum from tin, antimony, and arsenic, compare § 157, 13.

† Compare the notes in Section III.

and nitric acid is gradually added, with continued heating and constant stirring. A great excess of acid is to be avoided.

1. THE PRECIPITATE DISSOLVES, AND THERE REMAINS FLOATING IN THE LIQUID ONLY THE SEPARATED, LIGHT, FLOCCULENT AND YELLOW SULPHUR: this indicates the absence of mercury. CADMIUM, COPPER, LEAD, and BISMUTH may be present. Filter from the separated sulphur, and treat the filtrate as follows, after freeing it from the greater part of the nitric acid by evaporation: To a portion of the filtrate add dilute sulphuric acid in not too small quantity, heat, and allow to stand some time. 126

a. NO PRECIPITATE FORMS: absence of lead. Mix the remainder of the filtrate with ammonia in excess. 127

α. No precipitate is formed: absence of bismuth. If the liquid is blue, COPPER is present; but very minute traces of copper might be overlooked if the color of the ammoniacal fluid alone were considered. To be quite safe, and also to test for cadmium, evaporate the ammoniacal solution nearly to dryness, add a little water and enough hydrochloric acid so that the liquid *only just* reacts acid, and 128

aa. Test a small portion for copper with potassium ferrocyanide. A reddish-brown precipitate or a light brownish-red turbidity indicates COPPER (in the latter case only to a very trifling amount). 129

bb. To the remainder, if copper is absent, after the addition of a little more hydrochloric acid, add hydrogen sulphide. A yellow precipitate indicates CADMIUM. If copper is present, on the other hand, it is most conveniently precipitated in the form of cuprous sulphocyanide, after the addition of some sulphurous acid, by means of potassium sulphocyanide; this is allowed to settle in a warm place, and the clear filtrate, after being evaporated to drive off the excess of sulphurous acid, and mixed with a little hydrochloric acid, is tested for cadmium with hydrogen sulphide. 130

Or both metals may be precipitated, after the addition of hydrochloric acid, with hydrogen sulphide, and the sulphides separated with potassium cyanide (in which case they must be freshly precipitated), or the sulphides may be separated by boiling dilute sulphuric acid (§ 143).*

β. A precipitate is formed: BISMUTH † is present. **131** Filter, and test the filtrate for copper and cadmium (and for any zinc present here) as directed in **128**. To test the washed precipitate more fully for bismuth, slightly dry between blotting-paper the filter containing it, remove the still moist precipitate with a platinum or glass spatula, dissolve on a watch-glass in the *least possible quantity* of hydrochloric acid, and then add water in not too small amount. The appearance of a milky turbidity confirms the presence of bismuth.

b. A PRECIPITATE IS FORMED BY SULPHURIC ACID: **132** presence of LEAD. Mix the whole of the nitric acid solution in a porcelain dish with dilute sulphuric acid in not too small amount, evaporate on the water-bath until the nitric acid is expelled, dilute the residue with some water containing sulphuric acid, filter off at once the lead sulphate left undissolved, and test the filtrate for bismuth, copper, and cadmium (and eventually for zinc and iron present here), according to **127**, ‡ and always test the precipitate, after washing it, by one of the methods described in § 143.

2. THE PRECIPITATE OF THE SULPHIDES DOES NOT COM- **133** PLETELY DISSOLVE IN THE BOILING NITRIC ACID, BUT LEAVES A

* If the precipitate obtained from acid solution with hydrogen sulphide contains zinc sulphide (compare the foot-note under **112**), the zinc is found in the liquid containing hydrochloric acid, from which the cadmium sulphide (and copper sulphide also, if present) is filtered, and from this solution it may be precipitated as white zinc sulphide by the addition of ammonia and, if necessary, ammonium sulphide.

† If the precipitate from acid solution by hydrogen sulphide should contain iron sulphide (compare the foot-note under **112**), the iron is present in the precipitate produced by ammonia (*β*), and may usually be recognized simply by the reddish-brown color. Confirm by testing a portion of the hydrochloric acid solution of this precipitate with potassium sulphocyanide.

‡ Concerning another course for detecting cadmium, copper, lead, and bismuth, see the third section of Part II, additions and notes to § 229.

RESIDUE, BESIDES THE SULPHUR THAT FLOATS IN THE FLUID: probable presence of MERCURIC SULPHIDE (which may be pronounced almost certain if the precipitate is heavy and black).* Allow the precipitate to subside, filter off the fluid, which is still to be tested for LEAD, BISMUTH, CADMIUM, and COPPER, and also for any zinc and iron present here; mix a small portion of the filtrate with a large amount of hydrogen sulphide water, and also, if no precipitate is produced thereby, with a little ammonium sulphide after the addition of ammonia, and should a precipitate form or a coloration become visible, treat the remainder of the filtrate according to 126.

Besides mercuric sulphide, the residue may also contain cadmium sulphide held back by mercuric sulphide, lead sulphate formed by the action of nitric acid upon lead sulphide, and, further, stannic oxide, and possibly gold and platinum sulphides. (The separation of the sulphides of tin, gold, and platinum from the sulphides of the metals of the fifth group is often incomplete). Wash this residue and examine a portion of it for MERCURY† by dissolving it in some hydrochloric acid, with the addition of a very small portion of potassium chlorate, and testing the solution with metallic copper or stannous chloride (§ 139). Warm the remainder of the residue with a concentrated solution of ammonium acetate, and exhaust it with this if a portion of the filtrate tested with hydrogen sulphide shows the presence of lead. Heat the residue which generally remains, after washing it, in a porcelain crucible with access of air, under a hood with a good draught, whereupon any mercuric sulphide present is volatilized. If a residue is left, heat it just to fusion with a mixture of equal parts of sodium carbonate and potassium cyanide, using a small flame, and

* If the sulphides (125) have been boiled with concentrated instead of dilute nitric acid, there is then formed, under certain conditions, instead of black mercuric sulphide, the white compound $2\,HgS.Hg(NO_3)_2$. (Compare § 139, 3.)

† If an aqueous solution, or a solution in very dilute hydrochloric acid, has been used, the mercury found was present in the original substance in the mercuric form; but if the solution has been prepared by boiling with concentrated hydrochloric acid, or by heating with nitric acid or aqua regia, the mercury may have been originally present in the mercurous form.

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treat the cool mass with water. If a metallic powder remains undissolved, wash this and warm it with concentrated hydrochloric acid, dilute, and test a part of the filtered liquid with mercuric chloride for tin. Mix the remainder with potassium or sodium hydroxide solution in moderate excess, filter off any white precipitate remaining undissolved, after washing the latter, dissolve it in hydrochloric acid, and test the solution with hydrogen sulphide for cadmium. If a residue remained upon treating the metallic powder with hydrochloric acid, warm it with aqua regia, and test the solution by § 151 for gold and platinum. Mix the aqueous solution of the fused mass, containing potassium cyanide, with hydrogen sulphide, because cadmium may be present in this also.

§ 230.*

Precipitation with Ammonia and Ammonium Sulphide: Separation and Detection of the Metals of Groups III and IV: Aluminium, Chromium, Zinc, Manganese, Nickel, Cobalt, Iron; and also of those Salts of the Alkali-Earth Metals which are precipitated by Ammonia from their Solutions in Hydrochloric Acid; Phosphates, Borates, Oxalates, Silicates, and Fluorides.

Since the precipitation by ammonia and ammonium sulphide serves the desired purpose with all the metals and salts just mentioned only when organic substances (especially those which are not volatile) are absent (for many, *e.g.*, citric acid, prevent the precipitation of aluminium and chromic hydroxides, of calcium phosphates, etc.), before passing on to the precipitation with ammonia and ammonium sulphide it is advisable in the first place to destroy organic substances if they are present, that is, if they were found in the preliminary examination (**10**). The two following cases are therefore to be distinguished:

A. Organic Substances are not present.

Put a *small portion* of the liquid in which hydrogen sulphide has failed to produce a precipitate or has pro- **134**

* Compare the notes in Section III.

DUCED ONLY A SEPARATION OF SULPHUR (110), OR OF THE LIQUID WHICH HAS BEEN FILTERED FROM THE PRECIPITATE FORMED (112), in a test-tube, observe whether it is colored or not,* boil to expel the hydrogen sulphide which may be present, add a few drops of dilute nitric acid, boil and observe the color of the liquid again. A change of color to yellow upon boiling with dilute nitric acid generally indicates iron, but it may also be due to the liberation of iodine. (In the latter case, the liquid has the odor of iodine, and must be freed from iodine or iodine chloride by evaporation on the water-bath, and then be diluted again before the addition of ammonia, for otherwise nitrogen iodide might form, which would separate as a brownish-black precipitate.) Now add ammonia carefully, just to alkaline reaction, heat, observe whether this alone produces a precipitate, and finally add some ammonium sulphide, whether ammonia has produced a precipitate or not.

a. NEITHER AMMONIA NOR AMMONIUM SULPHIDE PRODUCES A PRECIPITATE. Pass on to § 231, for iron, nickel, cobalt, zinc, manganese, chromium, aluminium, are not present, nor are phosphates, borates,† silicates, oxalates,‡ and fluorides of the alkali-earth metals; nor silicic acid, originally in combination with other metals. 135

b. AMMONIUM SULPHIDE PRODUCES A PRECIPITATE, AMMONIA HAVING FAILED TO DO SO: absence of phosphates, borates,† silicates, oxalates,‡ and fluorides of the 136

* If the fluid is colorless, it contains no chromium or only traces of it. If colored, the tint will, to some extent, act as a guide to the nature of the substance present. Thus a green or a violet tint, the latter turning green upon boiling, points to chromium; a light green tint, to nickel; a reddish color, to cobalt. It must, however, be remembered that these tints are perceptible only if the metals are present in large quantity, and also that complementary colors, such as the green of a nickel solution and the red of a cobalt solution, will destroy each other, and that, accordingly, a solution may contain both metals and yet appear almost colorless.

† The precipitation of alkali-earth metal borates is easily prevented by the presence of much ammonium chloride.

‡ Magnesium oxalate is precipitated by ammonia from hydrochloric acid solutions only after a long time, and never completely. Dilute solutions are not precipitated at all.

alkali-earth metals; of silicic acid, originally in combination with other metals; and also of iron, chromium, and aluminium. Pass on to **138**.

c. AMMONIA PRODUCES A PRECIPITATE before the addition of ammonium sulphide. The course to be pursued now depends upon whether (α) the original solution is simply aqueous, and has a neutral reaction, or (β) the original solution is acid or alkaline. In the former case pass on to **138**, since phosphates, borates, oxalates, silicates, and fluorides of the alkali-earth metals and silicic acid in combination with other metals cannot be present. In the latter case, if the solution was acid, regard must be had to the possible presence of all the bodies enumerated in **135**. Pass on, therefore, to **150**. If the original solution was alkaline, proceed also according to **150**, but in this case, consideration need be taken generally of silicic acid and aluminium and chromic phosphates only, because any of the salts of the alkali-earth metals enumerated in **135** can be present in alkaline liquids only very exceptionally. **137**

1. DETECTION OF THE METALS OF GROUPS III AND IV IF PHOSPHATES, ETC., OF THE ALKALI-EARTH METALS ARE NOT PRESENT.* **138**

Mix the fluid mentioned at **134**, a portion of which has been submitted to a preliminary examination, with some ammonium chloride, then with ammonia, *just* to alkaline reaction, lastly with ammonium sulphide until the fluid, after being shaken, smells distinctly of that reagent; shake the mixture until the precipitate begins to separate in flakes, heat gently for some time, and filter.

Keep the FILTRATE,† which contains or may contain

* This simpler method will fully answer the purpose in most cases; but for very accurate analysis, the method beginning at **150** is preferable, as this will also permit the detection of minute quantities of alkali-earth metals which may have been thrown down together with aluminium and chromic hydroxide. Solutions which are distinctly colored by chromic salts should always be examined by **150**.

† If the filtrate has a brownish color, this points to nickel, since this sulphide, under certain circumstances, as is well known, is slightly soluble in

metals of Groups II and I, for subsequent examination according to § 231. Wash the PRECIPITATE with water to which a very little ammonium sulphide has been added, then proceed with it as follows:

a. IT HAS A PURE WHITE COLOR: absence of iron, cobalt, nickel. Test it for all the other bases of Groups III and IV, as the faint tints of chromic hydroxide and manganese sulphide are imperceptible in a large quantity of a white precipitate. Dissolve the precipitate by heating it in a small dish with the least possible amount of hydrochloric acid; should hydrogen sulphide be evolved, boil until this is completely expelled, filter if necessary, concentrate by evaporation to a *small** bulk, add rather concentrated solution of sodium or potassium hydroxide in excess, and then boil for some time with constant stirring. **139**

α. The precipitate formed at first dissolves completely in the excess of soda: absence of manganese and chromium, presence of aluminium or zinc. Test a portion of the alkaline solution with a little hydrogen sulphide water (not an excess) for ZINC; acidify the remainder with hydrochloric acid, add ammonia *slightly* in excess, and apply heat. A white flocculent precipitate, insoluble in more ammonium chloride, indicates ALUMINIUM.† **140**

β. The precipitate formed does not dissolve, or dissolves only partially, in the excess of sodium hydroxide. Dilute, filter, and test the FILTRATE, as in **140**, for ZINC and ALUMINIUM. Wash the undissolved PRECIPITATE and dry it. If it is brown or brownish, MANGANESE is present in it; if the solution (of **141**

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ammonium sulphide. In this case, just acidify the liquid with acetic acid, heat for some time, filter off the separated nickel sulphide, and proceed with the filtrate according to § 231.

* Compare § 122, 6.

† The assumption that aluminium is present is of course only justified when the sodium or potassium hydroxide used was entirely free from alumina or silica. Since this is often not the case, a counter-experiment with nearly an *equal quantity* of the alkali alone may be made; if a very much smaller precipitate is now obtained than was obtained in the analysis, it may be concluded that aluminium is actually present in the substance.

the precipitate produced by ammonium sulphide) in hydrochloric acid is bluish-violet, CHROMIUM is present. With very small amounts of manganese, the color of the precipitate, and with very minute quantities of chromium, the color of the solution, are not to be recognized.

To test, therefore, for manganese and chromium 142
in the safest way, fuse the dried precipitate with sodium carbonate and potassium chlorate, and boil the mass with water. If the fused mass was yellow, or if the solution in water (which, in case it is green or red from potassium manganate or permanganate, is to be heated with a little alcohol) is yellow, then CHROMIUM is present. If the presence of MANGANESE cannot be decided upon with certainty from the green or red color of the fusion or its solution, then, in case an insoluble residue remained when the fusion was dissolved, test a portion of this with sodium carbonate in the oxidizing flame, for MANGANESE. If chromium is present, dissolve another portion of this residue in hydrochloric acid, for the detection of ZINC, which in that case may be present here, possibly in its whole amount (§ 128, 5); evaporate to a small volume, add sodium acetate, and mix with hydrogen sulphide water (§ 122, 4).

b. IT IS NOT WHITE: this indicates chromium, 143
manganese, iron, cobalt, or nickel. If it is black, or inclines to black, one of the last three metals is present. Under any circumstances, all the metals of Groups III and IV must be looked for.

With a spatula, or with the aid of a wash-bottle by washing it through a hole made in the bottom of the filter, remove the washed precipitate from the filter, and immediately pour over it cold hydrochloric acid diluted with hydrogen sulphide water (1 part of hydrochloric acid, 1.12 sp. gr., with about 5 parts of hydrogen sulphide water) in moderate excess.

α. It dissolves completely (except perhaps a little 144

sulphur): absence of cobalt and nickel, at least of notable quantities of these two metals.

Boil until the hydrogen sulphide is *completely* expelled, then add a little nitric acid, boil again, filter if particles of sulphur are suspended in the fluid, concentrate by evaporation to a *small* residue, add concentrated solution of potassium or sodium hydroxide in excess, boil for some time with constant stirring, dilute, filter the fluid from the insoluble precipitate which is sure to remain, wash the latter, and proceed to examine the filtrate, and then the precipitate.

aa. Test a small portion of the *filtrate* with a small amount of hydrogen sulphide water, for ZINC; acidify the remainder with hydrochloric acid, then test with ammonia, for ALUMINIUM. (Compare **140.**) **145**

bb. Dissolve a small portion of the *precipitate* in hydrochloric acid, and test with potassium ferrocyanide, added drop by drop, or with potassium sulphocyanide, for IRON.* Test the rest of the precipitate for MANGANESE, CHROMIUM, and (if chromium is present) for ZINC, according to **142.** In making the latter test, iron, if present, is to be precipitated by adding ammonia in excess, and the filtrate, after being acidified with acetic acid, is tested for zinc with hydrogen sulphide. **146**

β. The precipitate is not completely dissolved, a black residue being left: this indicates COBALT and NICKEL.† This indication is not quite certain, espe- **147**

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*Since Prussian blue dissolves in potassium ferrocyanide to a colorless liquid, small quantities of iron may be easily overlooked if the reagent is added rapidly in large quantity. The original solution must be tested with potassium ferricyanide and potassium sulphocyanide to learn whether the iron was present as a ferrous or ferric salt.

† This conclusion is justified only when the precipitation with hydrogen sulphide in **112** has been properly conducted, and especially when it has not been made from a solution which was too acid, for if the metals of Group V have not been completely precipitated by hydrogen sulphide, portions of them, especially of lead and cadmium, are found here.

cially in the presence of much ferrous sulphide, particles of which may become enveloped in the separated sulphur, and thus be protected from the action of the hydrochloric acid. Filter, wash, and examine the filtrate according to **144**.

Heat the precipitate with the filter in a porce- **148** lain crucible till the filter is incinerated. Warm the residue with some hydrochloric acid with the addition of a few drops of nitric acid, add some water, then ammonia in moderate excess, and filter from any ferric hydroxide which may have separated.

The ammoniacal filtrate is blue in the presence of much nickel, brownish in the presence of much cobalt, and has a less distinct, mixed color if both metals are present. Test a portion of it with ammonium sulphide, and if a black precipitate is formed, the presence of cobalt or nickel is proved.

In that case, evaporate the rest of the ammoniacal solution to dryness, drive off the ammonium salts by gentle ignition, and proceed with the residue as follows :

aa. Test a small portion of it with borax, first in the outer, then in the inner, gas or blowpipe flame. If the bead in the oxidizing flame is violet while hot, and is pale reddish-brown when cold, and in the reducing flame turns gray and turbid, NICKEL is present; but if the color of the bead is blue in both flames, whether hot or cold, COBALT is present. As, in the latter case, the presence of nickel (and in the presence of much nickel, traces of cobalt) cannot be distinctly recognized, examine

bb. The remainder of the residue by dissolv- **149** ing it in some hydrochloric acid, with the addition of a few drops of nitric acid, evaporating nearly to dryness, adding sodium carbonate until the reaction is alkaline, after that, acetic acid until the precipitate formed is dissolved and some excess of acetic acid is present besides, and

finally potassium nitrite in large quantity. If, after standing for some time at a gentle heat, a yellow precipitate forms in the solution which is acid with acetic acid, this confirms the presence of COBALT. Filter after about twelve hours, and test the filtrate with sodium hydroxide for NICKEL.*

2. DETECTION OF THE METALS OF GROUPS III AND IV IN CASES WHERE PHOSPHATES, BORATES, OXALATES, SILICATES, FLUORIDES OF THE ALKALI-EARTH METALS, OR SILICIC ACID MAY POSSIBLY HAVE BEEN THROWN DOWN, *i.e.*, in cases where the original solution was acid (or, under certain conditions, alkaline, compare **137**), and a precipitate was produced by ammonia in the examination at **134**. **150**

Mix the fluid mentioned in **134** with some ammonium chloride, then with ammonia just to alkaline reaction, lastly with ammonium sulphide, until the fluid, after being shaken, smells distinctly of the reagent; shake the mixture until the precipitate begins to separate, heat gently for some time, and filter.

Keep the FILTRATE,† which may contain bases of Groups II and I, for subsequent examination, according to § 231.

Wash the PRECIPITATE with water to which a very little ammonium sulphide has been added, then proceed with it according to the following course:

To obtain a clear idea of the obstacles to be overcome in this analytical process, it must be considered that it is necessary to examine the precipitate for the following bodies: iron, nickel, cobalt (these show their

* If so little nickel and cobalt were present that their sulphides went into solution completely in the treatment of the ammonium sulphide precipitate with a mixture of hydrochloric acid and hydrogen sulphide water (**143**), then they are present in the precipitate mentioned in **146**. They may be detected in the latter by dissolving a portion of it in hydrochloric acid, adding ammonia in excess, warming, filtering, acidifying the filtrate with acetic acid, adding sodium acetate, and passing in hydrogen sulphide while heating. A precipitate thus formed may contain zinc sulphide in addition to the slight amounts of cobalt and nickel sulphides, and if this is now treated again according to **143**, the latter remain behind.

† Should this be brown in consequence of containing nickel, proceed according to the second foot-note under **138**, p. 493.

presence to a certain extent by the black or blackish color of the precipitate), manganese, zinc, also chromium and chromium phosphate (the latter generally reveal their presence by the color of the solution), aluminium and aluminium phosphate, barium, strontium, calcium, and magnesium. The latter metals may have fallen down in combination with phosphoric acid, boric acid, oxalic acid, silicic acid, in the form of fluorides, or in combination with chromic oxide. Besides these bodies, silicic acid and free sulphur may be present.*

As the original substance must be afterwards exam- 151
ined for all acids that might possibly be present, it is not *indispensable* to test for the acids mentioned above at this stage; still, as it is often interesting to detect these acids at once, especially in cases where a somewhat large proportion of some alkali-earth metal has been found in the ammonium sulphide precipitate, a method for their detection will be given after that of the metals.

As soon as the washing is finished, remove the pre- 152
cipitate from the filter with a spatula, or with the washing-bottle, and pour over it in moderate excess a mixture of hydrochloric acid and hydrogen sulphide water (1 part of hydrochloric acid, sp. gr. 1.12, with about 5 parts of hydrogen sulphide water).

a. A RESIDUE REMAINS. Filter, and treat the fil- 153
trate as directed in **154**. If black, the residue may contain sulphides of nickel and cobalt, and, besides these, sulphur and silicic acid, possibly also calcium fluoride (which is rather difficultly soluble in hydrochloric acid). Wash the precipitate, and warm a part of it with hydrochloric acid, with the addition of nitric acid, evaporate to dryness, and treat the residue with hydrochloric acid and water. If it contains SILICIC ACID, this remains undissolved. Test the solution, or the filtrate from silicic acid, for NICKEL and COBALT, according to **148**. Incinerate the

* That sulphides of Group V may be also present here when the precipitation with hydrogen sulphide has been improperly conducted, is shown in the foot-note under **147**.

rest of the residue with the filter-paper, and test it for FLUORINE; in the absence of silicic acid, by § 176, 5, and in its presence by § 176, 6. If fluorine is found, test for CALCIUM the residue remaining after the treatment with sulphuric acid, by treating it with a little water, filtering, and adding an equal volume of alcohol (compare § 102, 3).

b. NO RESIDUE IS LEFT (except a little sulphur, whose purity is to be proved by washing, drying, and burning): absence of nickel and cobalt, at least in any notable proportion. **154**

Boil the solution until the hydrogen sulphide is expelled, filter if necessary, and then proceed as follows:

α. Mix a small portion of the solution with dilute sulphuric acid, and warm gently for some time. **155**

aa. No precipitate forms. In this case, add 1 or 2 volumes of alcohol. If a white precipitate is produced, it is due to CALCIUM SULPHATE. Filter it off, digest it with water, and confirm by adding ammonium oxalate to the filtered solution.*

bb. A precipitate is produced by dilute sulphuric acid: this may be BARIUM and STRONTIUM SULPHATES, and possibly CALCIUM SULPHATE. Filter it off, and proceed with the filtrate as in *aa.* Wash the precipitate, decompose it by fusion with sodium-potassium carbonate, then wash the carbonates, dissolve them in nitric acid, evaporate to dryness, and test the residue by **163.**

β. Heat a larger portion with some nitric acid, and test a small portion of the cooled solution with potassium ferrocyanide, added drop by drop, or with potassium sulphocyanide, for IRON.† Mix **156**

* Since the precipitated calcium sulphate may also contain small traces of strontium sulphate, it is advisable, in accurate analyses, to use the precaution of testing any residue left upon digestion with water for strontium by means of the spectroscope (§ 101, 8).

† Whether a ferrous or a ferric compound was present must be determined

the whole of the remainder with enough ferric chloride so that a drop mixed with ammonia upon a watch-glass gives a yellow precipitate;* evaporate the liquid (best on the water-bath) to a very small volume, transfer it by the aid of a little water to a flask, then add sodium carbonate solution until the free acid is *almost* neutralized, and finally to the still clear solution add barium carbonate in some excess, shake, and let the mixture stand in the cold until the liquid above the precipitate has become colorless. Filter the precipitate (*aa*) from the solution (*bb*) and wash it.

aa. Boil the *precipitate* for some time with 157
solution of sodium or potassium hydroxide, filter, and test the filtrate for ALUMINIUM,† by acidifying with hydrochloric acid, adding ammonia to alkaline reaction, and boiling. The part of the precipitate insoluble in sodium hydroxide is examined for CHROMIUM, by fusing with sodium carbonate and potassium chlorate, and treating the mass with water (§ 107, 10).

bb. Mix the *solution* first with a few drops of hydrochloric acid, boil (to remove all the carbonic acid), and then add some ammonia and ammonium sulphide.

αα. No precipitate forms: absence of man- 158
ganese and zinc. Mix the solution, which contains barium chloride, with dilute sulphuric acid in slight excess, boil, filter, make alkaline with ammonia, and add ammonium

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by testing the original solution in hydrochloric acid with potassium ferricyanide and with potassium sulphocyanide.

* The addition of ferric chloride is necessary in order to effect the certain separation of any phosphoric and silicic acids that may be present. These then go into the precipitate produced by barium carbonate, as do also oxalic acid, boric acid, and fluorine.

† If the solution or the sodium or potassium hydroxide which is used contains silicic acid, the precipitate assumed to be alumina may be silica. If this is surmised, ignite the probable alumina precipitate upon the cover of a platinum crucible, add to it a little potassium disulphate, fuse, and treat with hydrochloric acid and water. Alumina is then dissolved, leaving silica undissolved, and may be precipitated from the solution with ammonia.

oxalate solution. If a precipitate of CALCIUM OXALATE is formed, filter it off, and test the filtrate for MAGNESIUM with ammonium sodium phosphate and ammonia.

ββ. A precipitate forms. Filter, and pro- 159
ceed with the filtrate according to 158. The precipitate may contain zinc and manganese sulphides and traces of cobalt and nickel sulphides. Wash it and test for MANGANESE, ZINC, COBALT, and NICKEL, according to 143 to 150 (if the last two metals have not been found in 153).

γ. If alkali-earth metals have been found in *α* and 160
β, and it is desired to detect the acids in combination with which they have passed into the precipitate produced by ammonium sulphide, make the following experiments with the remainder of the hydrochloric acid solution of the precipitate produced by ammonia and ammonium sulphide. It is to be noticed, however, that phosphoric and silicic acids may also go into this precipitate (150) in combination with aluminium or chromium.

aa. Evaporate a small portion in a dish or watch-glass, on the water-bath, to complete dryness, then treat with hydrochloric acid. If there was any SILICIC ACID in the solution, this will be left undissolved. Then evaporate the solution with nitric acid, and test it for PHOSPHORIC ACID by means of molybdic acid solution (§ 172, 10).

bb. Concentrate another portion by evaporation, mix it with sodium carbonate solution *in excess*, boil for some time, filter, and examine one portion of the filtrate for OXALIC ACID, by acidifying with acetic acid and adding solution of calcium sulphate; another portion for BORIC ACID, by slightly acidifying with hydrochloric acid, and testing with turmeric-paper (§ 175, 5 and § 174, 5).

cc. Precipitate the remainder with ammonia, filter, wash, and dry the precipitate, and examine

it for FLUORINE according to § 176, 5, or, if required, § 176, 6.

B. Organic Substances are Present.

In this case divide the liquid in which hydrogen sul- 161
phide has produced no precipitate (110), or that which has been filtered from such a precipitate (112), into two unequal parts, consisting of about two thirds and one third. The smaller part will serve for testing for the alkali metals according to § 233; the larger part, after destroying the organic substances, is to be used for detecting the metals and salts enumerated at the beginning of § 230, and also the alkali-earth metals. Evaporate the larger part almost to dryness, add sodium carbonate in slight excess, and also some potassium nitrate, heat in a platinum vessel until the organic substances are just destroyed, soften the mass with water, and, in a glass or porcelain vessel, add hydrochloric acid to it, heat (if the solution is yellow from chromic acid, with the addition of some alcohol; § 166, 5), and then proceed with the solution thus obtained, according to **134**.

§ 231.*

Separation and Detection of those Metals of Group II, which are precipitated by Ammonium Carbonate in Presence of Ammonium Chloride, viz., Barium, Strontium, and Calcium.

Before continuing the examination it should be considered whether an ordinary analysis is required, or a very exact one in which even very small traces of alkali-earth metals ought not to be overlooked. For ordinary analyses, the process A will suffice, while for very exact work, the method B is to be followed.

A. Process for Ordinary Analyses.

To a small portion of the liquid in which ammonia 162
and ammonium sulphide have failed to produce a precipitate (135), or of the liquid filtered from the precipitate formed, add ammonium chloride, if the solution

* Compare the notes in Section III.

CONTAINS NO AMMONIUM SALT, THEN AMMONIUM CARBONATE AND SOME AMMONIA, AND HEAT FOR SOME TIME VERY GENTLY (not to boiling).

1. No PRECIPITATE FORMS: absence of any notable quantity of barium, strontium, and calcium. To another portion, in order to detect any traces of them, add some ammonium sulphate (prepared by more than neutralizing dilute sulphuric acid with ammonia); if the fluid becomes turbid, it contains traces of barium. To a third portion add some ammonia and ammonium oxalate; if the fluid turns turbid, perhaps only after standing, traces of calcium are present. Treat the remainder of the fluid as directed in § 232, after having removed, by means of the reagents that have served for their detection, any traces of calcium and barium which have been found.

2. A PRECIPITATE IS FORMED: presence of CALCIUM, 163
BARIUM, or STRONTIUM. Treat the whole fluid of which a portion has been tested with ammonia and ammonium carbonate in the same way as the portion; after gently heating, filter off the precipitate formed, and test portions of the filtrate with ammonium sulphate and oxalate for traces of calcium and barium, which it may possibly still contain; remove such traces, should they be found, by means of the same reagents, and examine the liquid (thus perfectly freed from barium, strontium, and calcium) for magnesium, according to § 232. Wash the precipitate produced by ammonium carbonate with water containing a little ammonia, dissolve it in the least possible amount of dilute nitric acid, evaporate the solution almost to dryness on the water-bath, then, at a somewhat higher temperature, upon the sand-bath, with continual stirring, until the residue no longer smells of nitric acid, and a cold glass plate placed over it for a moment no longer shows a deposit of moisture. After cooling, triturate the residue quickly, pour upon it (in a dry flask which is to be corked at once) from five to ten times its amount of a mixture of equal parts of ether and absolute alcohol, shake frequently, filter after one or two hours, using a filter-paper which is not wet with water, and wash any residue remaining with small quantities of the ether-alcohol mix-

ture until the last washings remain clear with a drop of dilute sulphuric acid.

164 *a. No residue remains:* absence of barium and strontium. Add a few drops of dilute sulphuric acid to the ether-alcohol solution. A precipitate shows the presence of CALCIUM.

165 *b. A residue remains.* Test the ether-alcohol solution as in *a*. Dissolve the residue with the aid of heat in 70 to 100 parts of water, filter if necessary, acidify with three or four drops of acetic acid, heat to boiling, add normal potassium chromate until the liquid shows a yellow color, and boil up again. Should there still be a perceptible odor of acetic acid, some more potassium chromate must be added.

α. No precipitate is formed: absence of barium. Mix the solution with ammonia and ammonium carbonate. A white precipitate shows STRONTIUM.

β. A light yellow precipitate forms immediately or after standing for a while: presence of BARIUM. Filter after an hour, and test the filtrate according to *α* for STRONTIUM.

B. PROCESS FOR VERY EXACT ANALYSES.

166 *a.* Since the precipitation of barium, strontium, and calcium by means of ammonium carbonate is interfered with by *large* amounts of ammonium salts, the latter must be removed, in case they were originally present or have been introduced into the liquid by the previous operations, before testing for the alkali-earth metals. Therefore, either evaporate directly to dryness the liquid which has been tested with ammonia and ammonium sulphide with negative results (135) or add hydrochloric acid to the liquid which has been filtered from the precipitate obtained with ammonia and ammonium sulphide, heat it to boiling for some time, filter off the sulphur, and then evaporate this filtrate to dryness. In either case, remove the ammonium salts by heating, moisten the residue with hydrochloric acid, add water and ammonia, filter, and proceed with the filtrate according to 162.

b. Since, in case the extraction of the nitrates with ether and alcohol (163) has not been complete, small amounts of calcium nitrate may have remained in the residue, the precipitate obtained by ammonia and ammonium carbonate in **165**, *α*, if it is very small, may be calcium carbonate. Test this spectroscopically, therefore, for strontium (§ 101, 8), or by the method described in § 104.

c. Since, if the operation has not been quite correctly carried out, traces of strontium may be contained in the ether-alcohol solution tested in **164**, examine the precipitate produced by sulphuric acid, in case it is small, either by the help of the spectroscope (§ 102, 8), or according to the method given in § 104, to find if it is really calcium sulphate.

§ 232.

Examination for Magnesium.

TO A PORTION OF THE LIQUID IN WHICH AMMONIUM CARBONATE, SULPHATE, AND OXALATE HAVE FAILED TO PRODUCE A PRECIPITATE (**162**), OR OF THE LIQUID FILTERED FROM THE PRECIPITATES FORMED (**163**), ADD AMMONIUM CHLORIDE, IF AMMONIUM SALTS ARE NOT PRESENT, THEN AMMONIA AND SOME SODIUM AMMONIUM PHOSPHATE, AND, IF A PRECIPITATE DOES NOT FORM AT ONCE, RUB THE INNER SIDES OF THE TEST-TUBE WITH A GLASS ROD, AND LET THE MIXTURE STAND FOR SOME TIME.

1. NO PRECIPITATE IS FORMED: absence of magnesium. **167** Pass on to § 233.

2. A CRYSTALLINE PRECIPITATE IS FORMED: presence of MAGNESIUM. To test for the ALKALI METALS, pass on to § 233. Ammonium magnesium phosphate is always crystalline, and if, therefore, ammonium sodium phosphate produces a slight, flocculent precipitate, it is not justifiable to assume the presence of magnesium. The slight, flocky precipitate which is sometimes thrown down here may be aluminium phosphate. It is obtained when alumina was present, and when too great an excess of ammonia was used in precipitating the metals of Groups III and IV.

Its appearance depends upon the circumstance that aluminium phosphate is less soluble than aluminium hydroxide in ammonia solution. Aluminium phosphate differs from ammonium magnesium phosphate in its insolubility in acetic acid. In order to confirm the presence of magnesium, a flocculent precipitate obtained by ammonium sodium phosphate should therefore, after filtering, be treated with a little acetic acid, and the resulting filtrate (which must not be made turbid by ammonium sulphate and oxalate) mixed with ammonia and a few drops of ammonium sodium phosphate. If magnesium is present, a crystalline precipitate is now obtained.

§ 233.

Examination for Potassium and Sodium.

The following liquids may be in hand for testing for potassium and sodium:

1. IN THE ABSENCE OF ORGANIC SUBSTANCES:

a. The remainder of the solution tested for magnesium with a negative result (§ 232, 1).

b. The remainder of the solution tested for magnesium with a positive result (§ 232, 2).

2. IN THE PRESENCE OF ORGANIC SUBSTANCES: the third of the liquid reserved in **161**, in which hydrogen sulphide has produced no precipitate (**110**), or that filtered from the resulting precipitate (**112**).

According as one or another of these liquids is at hand, a varying preparatory treatment is necessary.

α. Case 1, *a.* **168**

Evaporate to dryness a sample of the solution tested for magnesium in § 232, 1, with a negative result (conveniently in the hollow of a platinum crucible cover), and ignite gently. If no residue remains, potassium and sodium are not present. Pass on to § 234. If a residue remains, treat all the rest of the solution in a platinum or porcelain dish in the same way as the sample, and proceed with the residue, thus freed from ammonium salts, by **169**.

β. Case 1, *b*.

Evaporate to dryness the remainder of the liquid tested in § 232, 2, for magnesium with a positive result, ignite until all the ammonium salts have been removed, heat the residue with some water, and add a few drops of barium chloride. If this produces a precipitate, add a little more barium chloride until everything capable of being thus precipitated has been thrown down, then, with continued heating, add barium hydroxide solution prepared from the crystals, or rather thin milk of lime (calcium hydroxide) which has been freed from all traces of alkalies by repeated extraction with water, until turmeric-paper is *strongly* colored brown. After boiling some time, filter, add to the filtrate a slight excess of ammonium carbonate to which some ammonia has been added, warm for some time gently, filter, and evaporate the filtrate to dryness, then ignite gently until all ammonium salts have been driven off. If no residue remains, potassium and sodium are not present. Pass on to § 234. If a residue does remain, proceed with it according to **169**.

γ. Case 2.

The liquid under consideration here contains organic substances, and possibly also all the metals and salts mentioned at the beginning of § 230, as well as all the alkali-earth metals. Evaporate it to dryness in a porcelain dish, moisten the residue with pure concentrated sulphuric acid, and heat under a good hood or in the open air until the greater part of this has evaporated. After cooling, add water, filter, mix the hot filtrate with barium chloride as long as a precipitate is still formed, then add barium hydroxide solution or milk of lime, and proceed as given in *β* (Case 1, *b*).

The residue obtained in *α*, *β*, or *γ*, freed from ammo- **169**
nium salts, should not be tested directly for the alkali metals, because it generally contains small amounts of the alkali-earth metals, and perhaps a little silicic acid. Dissolve it, therefore, in a little water, add some ammonia, and then a little ammonium carbonate, and warm gently for some time. If a precipitate has formed, filter it off. Evaporate this filtrate, or the liquid which has

remained clear, to dryness again, and ignite gently to remove the small amount of ammonium salts. If a residue now remains, potassium or sodium is present. Dissolve this in very little water, in which it must dissolve clear,* transfer half of the liquid to a watch-glass, leaving the other half in the porcelain dish.

aa. Add to the latter portion a few drops of *hydrochloroplatinic acid* solution. If a yellow, crystalline precipitate is formed at once or after some time, POTASSIUM is present. If no precipitate is formed, allow the liquid to evaporate at a gentle heat, and treat the residue with very little water (if only chlorides are present, still better with a mixture of water and alcohol). The slightest trace of potassium may then be recognized by the fact that a small amount of a heavy yellow powder remains undissolved (§ 94, 3). In the presence of an iodide, the deep brown color of the liquid interferes with the detection of potassium by hydrochloroplatinic acid (§ 97). Under these circumstances, it is better to test with sodium acid tartrate. 170

bb. To the other half, after testing its reaction and neutralizing any free acid with potassium carbonate, add some *acid potassium pyroantimonate.* If a crystalline precipitate is formed thereby, immediately or after some time, SODIUM is present. The complete absence of sodium can be assumed with certainty only if no crystals of acid sodium pyroantimonate have formed, even after twelve hours. In regard to the crystalline form of the precipitate, and the precautions to be taken in making the test, compare § 95, 2. 171

§ 234.

Examination for Ammonium.

THERE STILL REMAINS THE EXAMINATION FOR AMMONIUM. 172

Triturate some of the substance under investigation, or,

* If this is not the case, the above described purification from traces of the alkali earths or silicic acid must be repeated.

if a liquid is in hand, a portion of this, with an excess of calcium hydroxide, and, if necessary, a little water. If any escaping gas smells of ammonia, if it blues moist, red litmus-paper, and forms white fumes when a glass rod moistened with acetic acid is lowered into the vessel containing the mixture, AMMONIUM is present. The reaction is most sensitive if the trituration is made in a small beaker, and the latter covered with a glass plate, with a strip of moist turmeric- or red litmus-paper adhering to the under side.

Complex Compounds.

A. 1. SUBSTANCES SOLUBLE IN WATER.

DETECTION OF ACIDS.*

§ 235.

I. *In the Absence of Organic Acids.*

In the first place, consider which are the acids that 173
form compounds soluble in water with the bases found, and let this be the guide in the examination. To beginners, the table given in Appendix IV will prove of considerable assistance. The following method of analysis works best when the acids are combined exclusively with alkali metals. It is therefore usually advisable to precipitate other metals first, with sodium carbonate, with the application of heat, and then to examine the filtrate.

1. THE ACIDS OF ARSENIC, CARBONIC ACID, SULPHUR combined with metals or hydrogen, CHROMIC ACID, HYDROFERRICYANIC ACID, and SILICIC ACID will have been usually detected in the preliminary examination or in testing for the metals (see §§ 211, 225, 226, and 228). Chromic acid is also easily recognized by the yellow or reddish-yellow color of the solution. If in doubt, test for it with lead acetate with the addition of acetic acid (§ 166, 8).

2. Test the reaction of the liquid, and if it does not 174
react neutral, make a considerable portion of it *exactly*

* See the explanations in Section III. In relation to another course for the detection of the inorganic acids, compare H. TREY, Zeitschr. f. analyt. Chem., 33, 533.

neutral with nitric acid or ammonia. Should this produce a precipitate (possibly of silicic acid, magnesium hydroxide, etc.), it is to be filtered off. If carbonic acid is evolved upon neutralization, it is to be removed by boiling. Four portions of this liquid are to be used for 3, 4, 7, and 8.

3. A portion of the clear, neutral solution mentioned in 2 is mixed with barium chloride, or, if the solution contains lead, silver, or a mercurous salt, with barium nitrate. **175**

a. NO PRECIPITATE IS FORMED: absence of sulphuric, phosphoric, chromic, silicic, oxalic, arsenious, and arsenic acids, as well as of any considerable quantities of boric and hydrofluoric acids.* Pass on to **176**.

b. A PRECIPITATE IS FORMED. Dilute the liquid, and add hydrochloric acid, or, as the case may be, nitric acid. If the precipitate does not redissolve, or at least not completely, SULPHURIC ACID is present.

4. Add silver nitrate to another portion of the clear, neutral solution (see 2). **176**

a. NO PRECIPITATE IS FORMED. Pass on to **181**, for there is neither chlorine, bromine, iodine, cyanogen,† sulphocyanogen, ferro- and ferricyanogen, nor sulphur present; nor phosphoric, arsenic, arsenious, chromic, silicic, oxalic acids, nor boric acid if the solution was not too dilute.

b. A PRECIPITATE IS FORMED. Observe its color,‡ then add nitric acid, and shake the mixture. **177**

α. The precipitate dissolves completely: absence of chlorine, bromine, iodine, cyanogen, sulphocyano-

* If the solution contains an ammonium salt in somewhat considerable proportion, the non-formation of a precipitate cannot be considered a conclusive proof of the absence of these acids, since the barium salts of most of them (not the sulphate) are more or less soluble in presence of ammonium salts. The precipitation of barium borate is also very much interfered with or prevented by the presence of alkali-metal chlorides.

† That the cyanogen in mercuric cyanide is not indicated by silver nitrate has been mentioned in the foot-note under **73**.

‡ Chloride, bromide, cyanide, sulphocyanide, ferrocyanide, oxalate, silicate, and borate of silver are white; iodide, orthophosphate, and arsenite of silver are yellow; arsenate and ferricyanide of silver are brownish-red; silver chromate is purple-red; and silver sulphide is black.

gen, ferro- and ferricyanogen, and also of sulphur. Pass on to 181.

β. A residue is left: chlorine, bromine, iodine, 178
cyanogen, sulphocyanogen, ferro- or ferricyanogen may be present; and if the residue is black or blackish, HYDROGEN SULPHIDE or a soluble METALLIC SULPHIDE. If necessary, the presence of sulphur may be readily confirmed, by mixing another portion of the solution with a solution of lead acetate in sodium hydroxide.

aa. Test another portion of the original solution, or of the solution precipitated with sodium carbonate, for IODINE, and subsequently for BROMINE, with starch paste and carbon disulphide, a solution of nitrous acid in sulphuric acid, and chlorine-water, according to p. 377, but compare also *cc.*

bb. Test a small portion of the liquid men- 179
tioned in *aa*, after the addition of some hydrochloric acid, with ferric chloride. A red color shows SULPHOCYANOGEN; a blue precipitate, FERROCYANOGEN. If the latter is obtained, shake another portion of the liquid mentioned in *aa* with ether, after the addition of some hydrochloric acid, pour off the layer of ether, and test it with ferric chloride for SULPHOCYANOGEN. If the color of the silver precipitate leads to the suspicion of the presence of FERRICYANOGEN, test another portion for the latter substance with ferrous sulphate (freshly prepared, by warming iron wire with dilute sulphuric acid in excess).

cc. CYANOGEN, if present in the form of a simple cyanide of an alkali metal soluble in water, may usually be readily recognized by the smell of hydrocyanic acid, which the substance emits, and which is rendered more strongly perceptible by the addition of a little dilute sulphuric acid. If ferrocyanogen and ferricyanogen are absent, cyanogen may be detected in the liquid men-

tioned in *aa*, by the method given in § 185, 6. If they are present, see § 188.

Since hydrocyanic acid seriously interferes with the detection of iodine and bromine by means of nitrous acid or chlorine-water and carbon disulphide, negative results obtained by testing in *aa*, in the presence of cyanogen, do not justify the conclusion that iodine and bromine are absent. In this case, it is necessary to destroy the cyanogen before testing for them, and for this purpose proceed as directed in § 188.

dd. Should bromine, iodine, cyanogen, sul- 180
phocyanogen, ferrocyanogen, ferricyanogen, and sulphur not be present, the precipitate which nitric acid has failed to dissolve consists of SILVER CHLORIDE.

But where one or more of these bodies are present, a special examination for chlorine may sometimes become necessary, particularly when the relative quantities of the precipitates do not afford a decided indication of the presence of chlorine.* In these rare cases, make use of one of the methods given in § 188.

5. CHLORIC ACID is known by the yellow color produced 181
when a little of the original solid substance, or that obtained by evaporation, is brought into contact with concentrated sulphuric acid, upon a watch-glass (§ 194, 7).

6. NITRIC ACID is tested for with ferrous sulphate and sulphuric acid, in a portion of the original solution (§ 193, 6). This reaction is impeded or prevented by the presence of some other acids. If such were present, particularly chloric, chromic, hydriodic, or hydrobromic acids, they are first to be removed or destroyed. Chloric acid is destroyed by ignition (§ 195, near the e nd); chromic acid is reduced by sulphurous acid, chromic hydroxide being precipitated afterwards with ammonia; hydriodic

* Supposing, for instance, silver nitrate to have produced a copious precipitate insoluble in nitric acid, and the subsequent examination to have shown mere traces of iodine or bromine, the presence of chlorine may be held to be demonstrated without requiring additional proof.

and hydrobromic acids are removed by silver sulphate. Moreover, the reaction § 193, 13, serves the purpose.

PHOSPHORIC, BORIC, SILICIC, and OXALIC ACIDS, as well as HYDROFLUORIC ACID, are still to be tested for.

For the first four acids, test only in cases where both barium chloride and silver nitrate have produced precipitates in neutral solutions. (Compare, however, footnote to 175.)

7. Test for PHOSPHORIC ACID by adding to a portion of 182
the neutral solution (see 2) ammonia in excess, then ammonium chloride and magnesium sulphate. Very minute quantities of phosphoric acid are detected most readily by means of molybdic acid (§ 172, 10). Arsenic acid, if present, must be first separated by hydrogen sulphide, whichever method of testing is to be used, the solution being acidified, and kept at 70° during the passage of the gas.

8. To make a preliminary test for OXALIC and HYDROFLUORIC ACIDS, add calcium chloride to a fresh portion of the neutral solution prepared in 2, and if a precipitate is produced, add acetic acid. If no precipitate is obtained, or if one which is formed dissolves easily in acetic acid, oxalic and hydrofluoric acids are not present; in the other case, although it cannot be concluded that one of these acids is present, there is reason for testing for them. Test, therefore, portions of the original substance for oxalic acid,* by § 175, 7, and for fluorine according to § 176, 5. But, since the solutions of many oxalates are not precipitated by calcium chloride (§ 177), always test directly for oxalic acid* when heavy metals are present by § 175, 7.

9. Acidify slightly, with hydrochloric acid, a portion 183
of the original solution, or, if the case requires it, that which has been precipitated with sodium carbonate, then test for BORIC ACID, by means of turmeric-paper (§ 174, 5). Since chloric, chromic, and hydriodic acids impede or prevent the reaction, these, if present, must be removed or destroyed before testing for boric acid (compare § 235,

* If the substance contains carbonic acid, this is to be first removed by means of dilute sulphuric acid.

6). Any nitrous acid present, which also has an interfering action upon this test, may be destroyed by bromine in the acidified solution.

10. Should SILICIC ACID not yet have been found in the course of testing for the bases, acidify a portion of the liquid with hydrochloric acid, evaporate to dryness, and treat the residue with hydrochloric acid (§ 180, 2).

Complex Compounds.

A. 1. SUBSTANCES SOLUBLE IN WATER.

DETECTION OF ACIDS.

II. *In the Presence of Organic Acids.*

§ 236.

1. The examination for the INORGANIC ACIDS, including 184
oxalic acid, is made as described in § 235. As the tartrates and citrates of barium and silver are insoluble or at least difficultly soluble in water, tartaric acid and citric acid can be present only in cases where both barium chloride and silver nitrate have produced precipitates in the neutral fluid; still, in drawing this inference, bear in mind that these salts are slightly soluble in solutions of ammonium salts.

In testing for the organic acids, a solution is generally used which is freed from the metals of Groups II, III, IV, V, and VI, according to 173, and which, if required, is to be made exactly neutral with ammonia or hydrochloric acid. If carbonic acid is evolved in this operation, it is to be removed by heating for a short time, with repeated agitation. If the metals cannot be fully removed by sodium carbonate, as is often the case in the presence of a non-volatile organic acid, complete the separation according to the method described at the beginning of § 220. The cases will be distinctly specified where the solution thus prepared should not be used, but the *original* aqueous solution instead.

2. Make a portion of the sufficiently concentrated 185
liquid feebly alkaline with ammonia, add some ammo-

nium chloride, then calcium chloride in not too small amount, rub the walls of the vessel with a glass rod or shake vigorously, and let the mixture stand about two hours.

a. NO PRECIPITATE IS FORMED, EITHER AT ONCE OR AFTER THE LAPSE OF SOME TIME: absence of tartaric acid. Pass on to **186**.

b. A PRECIPITATE IS FORMED IMMEDIATELY, OR AFTER SOME TIME. Filter, and keep the filtrate for further examination according to **186**. Wash the precipitate, the formation of which does not in any way show the presence of tartaric acid, because it may be due also to calcium phosphate, oxalate, etc.; digest and shake it with solution of sodium hydroxide without applying heat, then dilute with a little water, filter, and boil the filtrate some time. If a precipitate separates, TARTARIC ACID is indicated. Filter hot, and test the precipitate according to § 197, 8 or 15.

3. Mix the fluid in which calcium chloride has **186**
failed to produce a precipitate, or that which has been filtered from the precipitate formed (in the latter case some more calcium chloride is to be added), with 3 volumes of alcohol, stopper the flask, and let it stand at the lowest possible temperature for severa hours.

a. NO PRECIPITATE IS FORMED: absence of citric, **187**
malic, and succinic acids. Pass on to **190**.

b. A PRECIPITATE IS FORMED. Filter, and treat the **188**
filtrate as directed in **190**. Treat the precipitate, after washing it with some alcohol, as follows:*

Suspend the precipitate in water, add a little hydrochloric acid, filter if necessary, add ammonia to the filtrate to strongly alkaline reaction, and then heat for some time to boiling, during which the reaction must remain alkaline.

α. IT REMAINS CLEAR: absence of citric acid. Add

* If the precipitate is very slight, it may possibly be due to a portion of tartaric acid which has remained in solution in the treatment according to **185**. Dissolve it, therefore, in a little hydrochloric acid, and repeat the operations described in **185** and **186**.

more alcohol, let the mixture stand for some hours at the lowest possible temperature, filter off the precipitate, which may contain calcium malate and succinate, wash it with a little alcohol, remove it from the filter, dry it in a porcelain dish until all the alcohol is driven off, * dissolve it in about 2 cc of strong nitric acid (of about 1.35 sp. gr.), and evaporate to dryness on the water-bath; put 2 cc more of the same nitric acid upon the residue, evaporate again to dryness, and repeat this evaporation with 2 cc of nitric acid still a third time. In this operation, any succinic acid present remains unchanged, while any malic acid is converted into oxalic acid, with evolution of carbonic acid. Boil the residue with a small excess of sodium carbonate solution, filter, just acidify a portion with acetic acid, and add a few drops of calcium chloride solution. If a white precipitate of calcium oxalate is formed, MALIC ACID is indicated. To test for succinic acid in this case, nearly neutralize the remainder of the alkaline liquid with hydrochloric acid, precipitate the slightly alkaline solution hot with calcium chloride added somewhat in excess, filter, and mix the filtrate with alcohol. A resulting precipitate necessitates testing further for SUCCINIC ACID. If the precipitate, washed with alcohol, is suspended in a little water, dilute sulphuric acid is added, this is extracted repeatedly with ether, and the ether is distilled off, the succinic acid is obtained as a residue (§ 205). If oxalic acid formed from malic acid was not present, the rest of the alkaline solution may be exactly neutralized with hydrochloric acid, and succinic acid may be tested for with ferric chloride (§ 202, 5).†

β. A HEAVY WHITE PRECIPITATE IS FORMED: pres- 189
ence of CITRIC ACID. Filter while boiling, and test the filtrate for malic and succinic acids, as in . To

* Oxalic acid would *also* be produced by the action of nitric acid upon any alcohol which was left behind.

† For other methods of separating malic acid from succinic acid, see § 200.

remove all doubt as to whether the precipitate is calcium citrate, redissolve it in a little hydrochloric acid, heat, make alkaline again with ammonia, and boil. The precipitate must now be thrown down again. (Compare § 198, 3.)

4. Heat the filtrate of **188**, or the liquid in which the addition of alcohol has failed to produce a precipitate (**187**), to expel the alcohol, neutralize *exactly* with hydrochloric acid, and add ferric chloride. **190**

a. NEITHER A PRECIPITATION NOR A COLORATION RESULTS: absence of salicylic and benzoic acids, as well as of any considerable amounts of acetic and formic acids. Pass on to **191** and **192**.

b. A FLESH-COLORED PRECIPITATE IS FORMED: BENZOIC ACID. For confirmation, treat it, after it has been washed, with a small amount of hydrochloric acid (§ 203, 2).

c. A VIOLET COLORATION IS PRODUCED: SALICYLIC ACID. Since, if this is intense, a possible precipitate of ferric benzoate cannot be seen, filter the liquid, and wash the filter-paper with water. If there remains a flesh-colored precipitate, it is due to benzoic acid, and is to be subjected to confirmatory testing according to *b*.

d. A more or less red coloration is produced. In this case, ACETIC ACID or FORMIC ACID is present in somewhat large amount. Filter, and proceed with any precipitate of ferric benzoate collected upon the the filter-paper, according to *b*. Heat the filtrate to boiling, just dissolve the resulting precipitate by adding hydrochloric acid drop by drop, and add several volumes of water. A violet coloration shows the presence of SALICYLIC ACID.

5. Evaporate a portion of the original aqueous solution to dryness (if acid, after previously making alkaline with sodium hydroxide), introduce the residue or a portion of the original dry substance into a test-tube, pour some alcohol over it, add about an equal volume of concentrated sulphuric acid, and heat to boiling. Evolution of the odor of acetic ether demonstrates the presence of **191**

ACETIC ACID. The odor is rendered more distinctly perceptible by shaking the cooling or cold mixture.*

6. Test for FORMIC ACID by *exactly* acidifying a portion of 192
the liquid prepared according to 184, with hydrochloric acid, and heating with mercuric chloride solution. A white turbidity from the separation of mercurous chloride shows the presence of formic acid (§ 207, 6). Confirm its presence further by silver nitrate and by mercurous nitrate (§ 207, 4 and 5).*

Complex Compounds.

A. 2. SUBSTANCES INSOLUBLE IN WATER, BUT SOLUBLE IN HYDROCHLORIC ACID, NITRIC ACID, OR AQUA REGIA.

DETECTION OF THE ACIDS.

I. *In the Absence of Organic Acids.*

§ 237.

In the examination of these compounds, attention must be directed to all inorganic acids, with the exception of chloric acid. Cyanogen compounds and silicates are not examined by this method. (Compare §§ 240 and 241.)

1. CARBONIC ACID, SULPHUR (in the form of metallic sul- 193
phides), ARSENIOUS, ARSENIC, and CHROMIC ACIDS, if present, have been found already in the examination for bases; NITRIC ACID, if present, has been detected in the preliminary examination, by the ignition in a glass tube (8, *cc*).

2. Mix a sample of the substance with 4 parts of pure 194
sodium-potassium carbonate, and should a metallic sulphide be present, add some sodium nitrate; fuse the mixture in a platinum crucible if there are no reducible me-

* In the presence of chromic or chloric acid, it is not possible to detect acetic and formic acids by the methods given. Where chromic acid is present, mix the original solution with some sulphuric acid, then shake with an excess of lead oxide, filter, add dilute sulphuric acid to the filtrate in moderate excess, and distil. Make the distillate alkaline with sodium hydroxide, evaporate almost to dryness, and test the residue by 191 and 192. Also, when organic acids of the first and second groups are present in large amount, it is advisable first to mix the liquid with sulphuric acid and subject it to distillation. In the presence of chloric acid, this is reduced according to § 194, 10.

tallic compounds present, or in a porcelain crucible if such compounds are present; boil the cooled mass with water, filter, and proceed with the filtrate for the detection of the acids, according to § 235.*

3. As the phosphates of the alkali-earth metals, and also aluminium phosphate, are only incompletely decomposed by fusion with an alkali-metal carbonate, it is always advisable, in cases where alumina or alkaline earths are present and phosphoric acid has not yet been detected (compare **160**), to dissolve a fresh sample of the substance in nitric acid, and test for PHOSPHORIC ACID with molybdic acid solution (§ 172, 10). In the presence of silicic or arsenic acid, prepare a solution with hydrochloric acid, separate the former by § 180, 3, the latter with hydrogen sulphide according to § 156, 3, filter, evaporate the filtrate almost to dryness, with addition of nitric acid, dilute with water containing nitric acid, and then test with molybdenum solution. **195**

4. If alkali-earth metals have been found in the examination for bases, and fluorine has not yet been detected (**160**), a separate portion should be tested for FLUORINE, by § 176, 5 or 6.

5. That portion of the substance which has been treated as directed in **194** can be tested for SILICIC ACID, only in cases where the fusion has been effected in a platinum crucible. When a porcelain crucible has been used, examine a separate portion by evaporating the hydrochloric or nitric acid solution (§ 180, 3). **196**

6. Examine a separate portion of the substance for OXALIC ACID by boiling with sodium carbonate (see **198**). Acidify the alkaline filtrate with acetic acid, and test with solution of calcium sulphate. If a white, pulverulent precipitate is formed, this indicates oxalic acid. Confirm by taking a fresh portion of the substance, removing carbonic acid, if necessary, by treating with dilute sulphuric acid alone, and then testing according to § 175, 7.

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* In the presence of a metallic sulphide, a separate portion of it must be examined for sulphuric acid, by heating it with hydrochloric acid, filtering, diluting the filtrate, and adding barium chloride.

Complex Compounds.

A. 2. Substances insoluble in Water, but soluble in Hydrochloric Acid, Nitric Acid, or Aqua Regia.

Detection of the Acids.

II. *In the Presence of Organic Acids.*

§ 238.

1. Conduct the examination for INORGANIC ACIDS according to § 237. 197

2. Test for ACETIC ACID, using the original solution, or, if the case requires it, the distillate obtained after the addition of sulphuric acid, according to § 206, 7. (Compare also the foot-note under 191.)

3. To a small portion of the substance in a watch-glass add a little dilute hydrochloric acid. If a residue remains, it should be tested for BENZOIC ACID and SALICYLIC ACID according to § 205. Any considerable quantity of these acids is most readily detected in this way, but a small quantity might completely dissolve. It is therefore necessary to take these acids into consideration in 198.

4. Boil a portion of the substance for a few minutes with a large excess of sodium carbonate solution, adding some of the solid substance if the solution is not strong; dilute, and filter from the precipitate. All the organic acids are now in the filtrate as sodium salts. Evaporate the filtrate to concentrate it, acidify with hydrochloric acid, filter off any salicylic or benzoic acid that may separate in this case, drive off carbonic acid by moderate heating and repeated shaking, and proceed by 185. If heavy metals or aluminium should have gone into the solution through the agency of organic acids, they should be removed according to the directions given at the beginning of § 220, before testing for the organic acids. 198

Complex Compounds.

B. Substances insoluble or sparingly soluble in Water, Hydrochloric Acid, Nitric Acid, and Aqua Regia.

Detection of the Bases, Acids, and non-metallic Elements.

§ 239.*

To this class belong the following bodies: 199

Barium sulphate, strontium sulphate, and calcium sulphate.†

Lead sulphate‡ and lead chloride.§

Silver chloride, silver bromide, silver iodide, and silver cyanide.‖

Silicic acid, and many silicates.

Native and ignited alumina, and many aluminates.

Ignited chromic oxide and chromic iron-ore (a compound of chromic oxide and ferrous oxide).

Ignited and native stannic oxide (tin-stone).

Some metaphosphates and some arsenates.

Calcium fluoride and a few other compounds of fluorine.

Sulphur.

Carbon.

Of these compounds, those printed in small capitals are more frequently met with. To the silicates, a special chapter (§§ 241–245) is devoted.

The substance is first subjected to the preliminary experiments described below in *a–e*, unless the quantity at disposal is too small, in which case, pass

* Compare the observations in Section III; and in relation to the cyanogen compounds insoluble in acids, see § 240.

† Calcium sulphate passes partially into the solution effected by water, and often completely into that effected by acids.

‡ Lead sulphate may pass completely into the solution effected by acids.

§ Lead chloride can only be found here if the precipitate insoluble in acids has not been thoroughly washed with hot water.

‖ Bromide, iodide, and cyanide of silver are decomposed by boiling with aqua regia, and converted into silver chloride; they can accordingly be found here only in cases where the operator has to deal with a substance which (as aqua regia has failed to effect its solution) is examined directly by the method here described.

on at once to **205**, bearing in mind, however, that the substance must be assumed to contain all the bodies mentioned.

a. Examine attentively the physical condition of the substance, to ascertain whether it is homogeneous or not, whether it is sandy or pulverulent, whether it has the same color throughout, or is made up of variously colored particles, etc. A microscope, or at least a lens, will be often found useful for this purpose. **200**

b. Heat a small sample in a glass tube sealed at one end. If brown fumes arise, and SULPHUR sublimes, this is, of course, a proof of the presence of that substance. **201**

c. If the substance is black, this indicates, in most cases, the presence of CARBON (charcoal, coal, bone-black, lamp-black, graphite, etc.). Heat a small sample on platinum foil with the blowpipe flame directed from below; if the black substance is consumed, it consisted of CARBON in some form. Graphite (which may be readily recognized by its property of communicating its color to the fingers, to paper, etc.) requires the aid of oxygen and a strong red heat for complete combustion. **202**

d. Heat for some time a small sample with a small fragment of potassium cyanide and some water, filter, and test half of the filtrate by acidifying with nitric acid, and the other half with ammonium sulphide. If the former produces a white precipitate, while the latter (provided that the amount of potassium cyanide was not too large) gives a brownish-black precipitate, it is shown that the substance contains a SILVER compound. **203**

e. If an undissolved residue has been left in *d*, wash this thoroughly with water, and if white, moisten it with ammonium sulphide; if it turns black, LEAD SALTS are present. If, however, the residue left in *d* is black, heat it with a concentrated solution of slightly acid ammonium acetate,* filter, **204**

* This is prepared by mixing ammonia solution, without the addition of water, with acetic acid until the liquid has a slight acid reaction.

and test the filtrate for LEAD, by means of sulphuric acid and with hydrogen sulphide.*

The results obtained by these preliminary experiments serve as a guide in the following course:

1. *a.* LEAD SALTS ARE NOT PRESENT. Pass on to **206.** **205**

b. LEAD SALTS ARE PRESENT. Heat the substance with a concentrated, slightly acid solution of ammonium acetate* to about 70°, pour the solution through a filter, and repeat the operation until the lead salt is completely dissolved. Test a portion of the filtrate with barium chloride for SULPHURIC ACID; a second and third portion by the addition of sulphuric acid in excess, and by hydrogen sulphide, for LEAD; and the remainder, after dilution with 20 parts of water and adding nitric acid, with silver solution for CHLORINE. If ammonium acetate has left a residue, wash this, and treat it as directed in **206.**

2. *a.* SILVER SALTS ARE NOT PRESENT. Pass on to **207.** **206**

b. SILVER SALTS ARE PRESENT. Digest the substance, which was free from lead or has been freed from it by extraction with ammonium acetate, repeatedly with potassium cyanide and water, at a gentle heat (in presence of sulphur, in the cold), until all the silver salt is removed. If a *residue* is left, wash this, and proceed with it according to **207.** After sufficient dilution, acidify the solution with nitric acid in the open air or under a good hood. The resulting precipitate is then filtered off. It must give METALLIC SILVER after washing and fusing with sodium carbonate in a cavity on charcoal (§ 135, 10). Whether the silver was originally combined with a halogen, and with which one of them, is determined according to **214.** Finally, test the liquid, filtered from the silver precipitate, with barium chloride for sulphuric acid.†

* The presence of lead in silicates (*e.g.*, in lead glass) cannot be detected in this way.

† The potassium carbonate usually present in potassium cyanide may have occasioned a partial or complete decomposition of any alkali-earth metal sulphates that were present.

3. *a.* SULPHUR IS NOT PRESENT. Pass on to **208.** **207**

b. SULPHUR IS PRESENT. Heat the substance, free from silver and lead, in a covered porcelain crucible until all the sulphur is expelled, and if a residue is left, treat this according to **208.**

4. Mix the substance, free from silver, lead, and sulphur, with 2 parts of sodium carbonate, 2 parts of potassium carbonate, and 1 part of potassium nitrate,* heat in a platinum crucible until the mass is in a state of calm fusion, and place the red-hot crucible on a thick, cold iron plate to cool. It will thus generally be possible to remove the fused mass from the crucible in a cake. If this does not succeed, heat the crucible again until the edges of the cake begin to melt. After complete cooling, put enough water into the crucible so that the cake is well covered, and warm a little with a flame held underneath. The cake is then loosened at once, if the crucible has no bruises (STÖCKMANN). Place the mass, or, if necessary, the crucible with its contents, in a beaker, soak the cake with water, apply heat, filter off the residue usually remaining, and wash it until the water running through no longer gives a precipitate with barium chloride. (Only the first washings are collected with the filtrate.) **208**

a. The solution so obtained contains the acids which were present in the substance decomposed by fusing. But, besides these acids, it may also contain such bases as are soluble in caustic alkalies. Proceed as follows: **209**

α. Test a small portion, after acidifying with hydrochloric acid, for SULPHURIC ACID, by means of barium chloride.

β. Test another portion, after acidifying with nitric acid, with molybdic acid solution for PHOS-

* Addition of potassium nitrate is useful even in the case of white powders, as it counteracts the injurious action of lead silicate (should any be present) upon the platinum crucible. In the case of black powders, the proportion of potassium nitrate must be correspondingly increased, in order that carbon, if present, may be consumed as completely as possible, and that any chromite present may be more thoroughly decomposed.

PHORIC and ARSENIC ACIDS (§ 172, 10 and § 156, 9). If a yellow precipitate is obtained, any arsenic acid is detected and removed in another portion of the solution, after making it acid with sulphuric acid and evaporating on the water-bath to a small volume, by means of hydrogen sulphide, and the filtrate is then tested again for phosphoric acid.

γ. Test another portion for FLUORINE (§ 176, 7).

δ. If the solution is yellow, CHROMIC ACID is present. To confirm, acidify a portion of the solution with acetic acid, and test with lead acetate.

ε. Acidify the remainder with hydrochloric acid, 210
evaporate to dryness, and treat the residue with hydrochloric acid and water. If a residue is left which refuses to dissolve even in boiling water, this consists of SILICIC ACID. Test the hydrochloric acid solution now in the usual way for those bases which, being soluble in caustic alkalies, may be present here, especially for stannic oxide and alumina.

b. Dissolve *the residue usually left in* **208** in hydro- 211
chloric acid (effervescence indicates the presence of alkali-earth metals, and a residue insoluble in hydrochloric acid is to be examined according to **213**), and test the solution for the bases as directed in § 226. If much silicic acid has been found in **210**, it is advisable to evaporate the solution of the residue to dryness, and to treat with hydrochloric acid and water, in order that the silicic acid remaining in the residue may also be removed as completely as possible. In relation to the alkalies that may be present in silicates, see **212**.

5. If it has been found in **4** that the substance insoluble 212
in acids contains a silicate, treat a separate portion of it according to **228**, to ascertain whether this silicate contains alkalies or not.

6. If a residue is still left undissolved upon treating 213
the residue obtained in **208** with hydrochloric acid (**211**), this may consist either of silicic acid which has separated, or of an undecomposed portion of barium sulphate, or

possibly stannic oxide remaining undissolved; or it may be calcium fluoride and, if it is dark-colored, chromite, as the last two compounds are only with difficulty decomposed by the method given in **208**. Attention should, therefore, be called to the fact that stannic oxide may always be detected by § 153, 11, and that calcium fluoride may be easily decomposed by sulphuric acid (§ 176, 5). The decomposition of chromite is easily accomplished by heating the fine powder to fusion with an equal amount of sodium peroxide, or also by mixing it with about 8 parts by weight of a mixture of 1 part of potassium chlorate and 3 parts of soda-lime, and exposing the mixture to a bright red heat for 1½ hours in a covered platinum crucible. In both cases, the mass contains the chromium as an alkali-metal chromate, which may be extracted with water. If stannic oxide was in the residue with chromite, it would be obtained in the above operations partly as an alkali-metal stannate in the aqueous solution of the fusion, and upon treating the insoluble residue from this with hydrochloric acid, partly as stannic chloride in the acid solution.

7. If the residue insoluble in acids contained silver **214**
(**206**,*b*), an attempt should be made to obtain information as to whether that metal was present in the original substance as an insoluble compound, and if so, in what combination it existed, or whether it was converted into silver chloride, bromide, iodide, or cyanide, in the operation of treating the substance with solvents. This attempt may fail, however, for, under certain circumstances, the question is scarcely to be decided by a mere qualitative analysis. This is easily understood if it is considered that, for example, when a mixture containing silver chloride and potassium iodide is treated with water, silver iodide and potassium chloride are obtained, and that mercuric iodide and silver nitrate yield mercuric nitrate and silver iodide when acted upon by water, etc.

In order to obtain this information as far as possible, extract the original substance with boiling water, then with dilute nitric acid, wash the undissolved residue with

water, and, in the first place, test a small sample of it for silver according to 203. If silver is present, proceed to ascertain the acid radical with which the metal is combined. This may be effected by treating the rest of the residue with finely granulated zinc and water, with addition of some dilute sulphuric acid, with frequent shaking, and filtering after a few hours. The filtrate may now be tested directly for chlorine, bromine, iodine, and cyanogen; or the zinc may first be thrown down with sodium carbonate, in order to obtain the acid radicals in combination with sodium.

SECTION II.

PRACTICAL COURSE IN PARTICULAR CASES.

I. Special method for the Decomposition of Cyanides, Ferrocyanides, etc., insoluble in Water, and also of Mixed Substances, insoluble in Water, containing such Compounds.*

§ 240.

The analysis of cyanogen compounds insoluble in water, especially ferrocyanides, etc., by the common method is often attended by the manifestation of such anomalous reactions that the analyst is easily misled. Moreover, acids often fail to effect the complete solution of these compounds. For these reasons, it is advisable to analyze them, and mixtures containing them,† by the following special method: 215

1. Boil the residue which has been freed from all soluble substances by treatment with water, with strong potassium or sodium hydroxide solution, and after a few minutes' ebullition, add some sodium carbonate; boil again for some time, dilute with water, and filter, in case there is a residue, and wash the latter.

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* Before making analyses according to this course, the operator should make himself familiar with the explanations in Section III which refer to this paragraph.

† Whether insoluble cyanogen or ferro- and ferricyanogen compounds, etc., are present or not is usually determined in the preliminary examination, from the fact that when ignited in the closed tube they give off cyanogen (but sometimes, however, they give off nitrogen only), and, if water is present, hydrocyanic acid and ammonia also, a residue of the metal mixed or combined with carbon being left behind. The insoluble ferro- and ferricyanides when boiled with hydrochloric acid yield decomposition products which are usually blue or green.

a. The residue, which is now free from cyanogen, unless the substance contains silver cyanide, is examined by the usual method, beginning at **37**.

b. The solution, which, if combinations of com- **216** pound cyanogen radicals (ferrocyanogen cobalticyanogen, etc.) are present, contains these combined with alkali metals, may also contain other acids, which have been separated from their bases by boiling with sodium carbonate, and lastly, also, such hydroxides as are soluble in caustic alkalies. Treat it as follows:

α. Carefully mix a portion of the alkaline liquid with hydrogen sulphide water.*

aa. No permanent precipitate is formed: absence of zinc and lead and also of other metals of the fourth and fifth groups (which might possibly have gone into the alkaline solution through the agency of organic matters), with the exception of mercury, whose sulphide may remain in solution in the sodium sulphide which is formed. Pass on to **217**.

bb. A permanent precipitate is formed. Add to a larger portion of the alkaline liquid (**216**) sodium sulphide, drop by drop, as long as it produces a precipitate, but avoid as far as possible any considerable excess. Heat moderately, filter, and treat the filtrate according to **217**. Heat the washed precipitate with dilute nitric acid, which may leave mercuric sulphide and lead sulphate behind, and examine the solution for the metals of the fifth and fourth groups according to the usual course. If an insoluble residue remains after heating with nitric acid, it is to be tested for mercuric sulphide and lead sulphate according to **133**.

* Adding solution of hydrogen sulphide, or conducting the gas into the fluid, until the mixture smells of the reagent (*i. e.*, until the sodium or potassium hydroxide has been converted into an alkali-metal hydrosulphide) must, of course, be avoided, since this might lead to the precipitation of the alumina which may be present in the alkaline solution, and even of sulphides of metals of the sixth group; precipitations which are not intended here.

β. Mix a small portion of the alkaline liquid in which hydrogen sulphide has given no precipitate, or of that from which the precipitate produced by sodium sulphide has been filtered, with dilute sulphuric acid just to distinct acid reaction, and add hydrogen sulphide in case the liquid does not smell of this substance, or does not smell strongly of it. 217

aa. No precipitate is formed, with the exception of sulphur which may possibly separate: absence of the metals of the sixth group, and also of mercury in *this* solution. Pass on to **218**.

bb. A precipitate is formed. Proceed with a larger portion of the liquid mentioned in **217** as with the small portion, filter off the resulting precipitate, wash it, and then examine it for mercury and the metals of the sixth group according to § 227. Examine the filtrate according to **218**.

γ. The liquid in which sulphides could not be precipitated either in the alkaline or acid solution, or that from which such have been precipitated, is still to be examined for those metals which form compound cyanogen radicals (iron, cobalt, manganese, chromium), and, besides these, for aluminium. It must also be tested for cyanogen, ferrocyanogen, cobalticyanogen, etc., and for other acids. Proceed, therefore, as follows: 218

aa. Use small samples of it for testing for acids according to § 235, or, if the case requires it, § 236. If the liquid was already acidified with sulphuric acid, the testing for acids must be made promptly; otherwise any hydroferrocyanic or hydroferricyanic acids present may decompose. To begin, test the acidified liquid with ferric chloride for ferrocyanogen* and with ferrous sulphate for ferricyanogen*. If the fluid

* It is to be remembered in this connection that ferricyanogen originally present may be converted into ferrocyanogen, not only by hydrogen sulphide, but also by bases, etc., which are capable of higher oxidation, *e.g.*, $K_6Fe_2(CN)_{12} + 2KOH + 2FeO = 2K_4Fe(CN)_6 + Fe_2O_3 + H_2O$.

contains hydrogen sulphide, the latter test is of course omitted here, because hydroferricyanic acid is converted by hydrogen sulphide into hydroferrocyanic acid, and in this case, it is advisable, before testing for other acids, to free the solution as far as possible from hydrogen sulphide by passing a rapid stream of air through it. Cobalticyanogen may be recognized by giving a greenish precipitate with nickel salts and white precipitates with zinc and manganese salts, which may be proved to contain cobalt by means of the borax bead.

bb. Evaporate almost to dryness another sample of the liquid mentioned in **218**, after acidifying it with dilute sulphuric acid, then add pure concentrated sulphuric acid, and heat under a good hood until the greater part of the free sulphuric acid has escaped. Dissolve the residue in water and test the solution for iron, manganese, cobalt, chromium, and aluminium, according to § 230.

δ. Test other portions of the liquid mentioned **219** in **216** (in case it was necessary to precipitate sulphides from it, and testing for sulphuric acid and ferricyanogen was consequently impossible in **218**, *aa*) for sulphuric acid, after the addition of hydrochloric acid, or, if required, nitric acid, with barium chloride or barium nitrate, as the case may be, and for ferricyanogen * by means of ferrous sulphate, with the subsequent addition of hydrochloric acid.

2. Decompose another portion of the original substance by continued heating with pure concentrated sulphuric acid, and test the residue, after removing all other bases, for the alkali metals.

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* Compare the foot-note under **218**, *aa*.

II. Analysis of Silicates.

§ 241.

Whether the substance is a silicate or contains one is ascertained by the preliminary blowpipe examination with sodium metaphosphate (20). 220

The analysis of silicates really differs from the usual course only in regard to the preparatory treatment required to separate the silicic acid from the bases, and to obtain the latter in solution.

The simple and double silicates are divided into two classes, which must be sharply distinguished here, because they require different methods of analysis, viz., (1) silicates readily decomposable by acids (hydrochloric, nitric, and sulphuric acids), and (2) silicates which are not, or only with difficulty, decomposed by acids. Many rocks consist of mixtures of the two classes.

To ascertain to which class a given silicate belongs, reduce it to a very fine powder, and digest a portion with hydrochloric acid at a temperature near the boiling-point. If this fails to decompose it, test another portion by long-continued heating with a mixture of 3 parts of concentrated sulphuric acid and 1 part of water. If this also fails, the silicate belongs to the second class. Whether decomposition has been effected by the acid may be generally learned from external indications, as a colored solution forms almost invariably, and the separated gelatinous, flocculent, or finely pulverulent silicic acid takes the place of the original heavy powder, which usually grated under the glass rod with which it was stirred. But whether the decomposition is complete, or extends only to one of the components of the rock, may be ascertained by boiling the separated silicic acid, after washing, in a solution of sodium carbonate. If perfect solution ensues, complete decomposition has been effected; if not, the decomposition is only partial. The results of these preliminary tests will show whether the silicate should be examined according to § 242, § 243, or § 244.

Before proceeding further, examine a portion of the

substance also for water, by heating it in a perfectly dry glass tube. If the substance contains hygroscopic moisture, it must first be dried at 100° for a long time. Apply a gentle heat at first, but ultimately an intense heat, by means of a gas lamp provided with a chimney, or with the blowpipe. A preliminary examination for fluorine may be also conveniently combined with this (§ 176, 8).

A. Silicates Decomposable by Acids.

§ 242.

*a. Silicates decomposable by hydrochloric or nitric acid.**

221 1. Mix the finely pulverized silicate with a little water to a uniform paste, then add moderately concentrated hydrochloric acid (or nitric acid), and digest at a temperature near the boiling-point until complete decomposition is effected. Filter off a small portion of the liquid,† evaporate the remainder to dryness, together with the silicic acid suspended therein, heat the residue at a temper ature but little if at all above 100°, with constant stirring, until hardly any more acid vapors escape, allow it to cool, moisten with hydrochloric acid, or, as the case may be, with nitric acid; afterwards add a little water, and heat gently for some time.

This operation effects the separation of the SILICIC ACID, and the solution of the bases in the form of chlorides or nitrates. Filter, wash the residue thoroughly, and examine the solution by the usual method, beginning at § 225, II or III. The residual silicic acid must always be tested, as it cannot under any circumstances be considered pure. It frequently contains titanic acid, occasionally barium sulphate, possibly strontium sulphate, and often a little alumina. It is best tested by repeated heating in a platinum dish with hydrofluoric and sulphuric acids, until all the silicic acid is removed in form of silicon fluoride. The residue is finally ignited,

* Nitric acid would be preferred to hydrochloric acid, if silver or lead compounds were present.

† Any arsenious acid present would volatilize by evaporation with hydrochloric acid.

fused with potassium disulphate, and then treated with cold water. If anything insoluble now remains, it is filtered off and tested according to § 104, for BARIUM (and strontium) SULPHATE. The dilute aqueous solution is tested by long boiling for TITANIUM, * (§ 118) and the clear liquid or the filtrate from the resulting precipitate is tested with ammonia for ALUMINIUM. (If there is a possibility that silver chloride may have separated with the silicic acid, digest a part of the latter with ammonia, filter, and test the filtrate by making it acid with nitric acid.)

2. As in silicates, and more particularly in those decom- 222
posed by hydrochloric acid, there are often found other acids or acid-forming elements, the following instructions must be attended to, that none of these substances may be overlooked:

α. CARBONATES are detected in treating with hydrochloric acid. SULPHIDES are often detected in the same operation; otherwise they may be tested for according to § 187, 8 or 9.

β. If the separated silicic acid is black, and turns white upon ignition in the air, this indicates the presence of CARBON or of ORGANIC SUBSTANCES. In presence of the latter, the silicates emit an empyreumatic odor upon being heated in the glass tube.

γ. Test the portion of the hydrochloric acid solution filtered off before evaporating, for SULPHURIC ACID, PHOSPHORIC ACID, ARSENIOUS ACID, and ARSENIC ACID; for sulphuric acid by diluting and adding barium chloride; for acids of arsenic by passing in hydrogen sulphide, first in the cold, then at 70° (§ 157, 12); for

* If the silicic acid has been separated by evaporation on the water-bath, only a part of the titanic acid will be found remaining with it; the rest (often the greater part) will pass into the hydrochloric acid solution, and will be precipitated by ammonia together with aluminium and ferric hydroxides. To find this part, fuse the dried precipitate with potassium disulphate, dissolve the fusion in cold water, filter if necessary, dilute largely, pass in hydrogen sulphide until all the iron is reduced to the ferrous state, and (without filtering off the sulphur) keep the fluid boiling for an hour with a constant current of carbonic acid passing through it. Filter, wash, and ignite; the sulphur will burn off, and titanic oxide will remain. Should it still contain iron, redissolve it by fusion with potassium disulphate and treatment with cold water, and precipitate by boiling with sodium thiosulphate.

phosphoric acid by adding nitric acid, evaporating to dryness on the water-bath, warming the residue with nitric acid, filtering, and adding molybdic acid solution. Where arsenic is found, phosphoric acid is tested for in the fluid filtered from the sulphide of arsenic.

δ. BORIC ACID is best detected by fusing a portion of the substance in a platinum spoon with potassium-sodium carbonate, boiling the fused mass with water, and testing the solution by § 174, 5. 223

ε. With many silicates, boiling with water is sufficient to dissolve the CHLORIDES present, which may then be readily detected in the filtrate by silver nitrate. The safest way, however, is to dissolve the mineral in dilute nitric acid, and test the solution with silver nitrate.

ζ. FLUORIDES, which often occur in silicates in greater or smaller proportion, may be detected by § 176, 6.

3. If the silicate contains iron, as is generally the case, it is still to be determined whether this exists in the ferrous or ferric state, or in both states of oxidation. For this purpose heat a sample of the finely pulverized substance, as far as possible with exclusion of air, with moderately concentrated hydrochloric acid, dilute, filter, and test with potassium ferricyanide and with potassium sulphocyanide (§ 126, 8, and § 127, 8). 224

b. Silicates which resist the action of hydrochloric acid, but are decomposed by concentrated sulphuric acid.

Heat the very finely pulverized mineral with a mixture of 3 parts of pure concentrated sulphuric acid and 1 part of water (best in a platinum dish), finally drive off the greater part of the acid, boil the residue with hydrochloric acid, dilute, filter, and treat the filtrate as directed in § 226, and the residue (which, besides the separated silicic acid, may contain also sulphates of the alkali-earth metals, etc.) as directed in § 242, 1, for the residue insoluble in acids. If it is wished to examine silicates of this class for acids and acid radicals, treat a separate portion of the substance according to § 243. 225

B. Silicates which are not decomposed by Acids.*

§ 243.

As the silicates of this class are most conveniently de- 226
composed by fusion with sodium-potassium carbonate, the portion so treated cannot, of course, be examined for alkali metals. The analytical process is therefore divided into two principal parts, a portion of the mineral being examined for the silicic acid and the bases, with the exception of the alkalies, while another portion is specially examined for the latter. The mineral must be examined for other acids by some further experiments.

1. *Detection of the silicic acid and all the bases, with the exception of the alkalies.*

Reduce the mineral to a very fine powder, mix this 227
with 4 parts of sodium-potassium carbonate, and heat the mixture in a platinum crucible by means of a gas-lamp or a Berzelius alcohol-lamp until the mass is in a state of calm fusion. Place the red-hot crucible on a thick, cold iron plate, and let it cool there, or treat it, if necessary, according to **208**, in order to remove the fused cake from the crucible. If this succeeds, break the mass to pieces, and keep a portion for the examination for acids. Put the remainder, or, if the mass still adheres to the crucible, the latter with its contents into a porcelain dish, pour on water, warm for some time until the mass is disintegrated, add hydrochloric acid, and warm until the mass is dissolved, with the exception of some silicic acid which separates in flocks. Remove the crucible from the dish if necessary, evaporate to dryness, and treat the residue exactly as directed in **221**.

2. *Detection of the alkalies.*

To effect this, the silicate must be decomposed by 228
means of a substance free from alkalies. The following methods are the most suitable:

* It will be understood, from what has been stated in § 241, that these are not decomposed by heating with hydrochloric and sulphuric acids in open vessels; but by heating them, reduced to a fine powder, in a sealed glass tube, with a mixture of 3 parts of concentrated sulphuric acid and 1 part of water, or with hydrochloric acid, to 200°–210°, most of them are decomposed, and may accordingly be analyzed also in this manner (Al. Mitscherlich).

a. DECOMPOSITION BY AQUEOUS HYDROFLUORIC ACID. Mix the finely pulverized substance with water in a platinum dish to a thin paste, add hydrochloric acid and hydrofluoric acid, and heat (in the open air, using care that the escaping vapors are neither breathed nor come in contact with the hands) until the silicate has dissolved; then add dilute sulphuric acid and evaporate until the hydrochloric acid, the hydrofluosilicic acid, and the hydrofluoric acid have completely escaped, and until only a small part of the sulphuric acid still remains. After cooling, dilute with water, heat to boiling, add barium chloride in slight excess, then milk of lime to alkaline reaction. After heating to boiling again, filter, mix with ammonium carbonate and some ammonia as long as a precipitate is formed, filter after an hour, and proceed to test for potassium and sodium according to **168**, *β*, and to test for lithium, cæsium, and rubidium, according to p. 145.

b. DECOMPOSITION WITH A FLUORIDE. Mix 1 part of the finely powdered substance with 5 parts of barium fluoride or of pure, finely powdered fluor-spar, or with 3 parts of ammonium fluoride, and then (in a platinum crucible) with enough concentrated sulphuric acid to form a thick paste, warm gently for some time (where the fumes will pass off in a good draught), and finally heat more strongly until nearly all the excess of sulphuric acid is expelled. Boil the residue with water, cautiously add barium chloride as long as it produces a precipitate, then milk of lime, etc., and proceed exactly as in *a*.

c. DECOMPOSITION BY MEANS OF BARIUM CARBONATE AND CHLORIDE. Mix 1 part of the very finely triturated powder with 3 or 4 parts of barium carbonate and 2 parts of barium chloride, heat the mixture as strongly as possible in a platinum crucible for half an hour, soften the mass with water, boil with the addition of a small amount of milk of lime, filter, precipitate with ammonium carbonate and ammonia, and proceed for the remainder of the process as in *a*. 229

[*d.* DECOMPOSITION BY MEANS OF CALCIUM CARBONATE AND AMMONIUM CHLORIDE. Mix 1 part of the pulverized substance with 1 part of powdered ammonium chloride and 8 parts of precipitated calcium carbonate. Expose the mixture to a moderate red heat in a covered platinum crucible for 30 or 40 minutes. Treat the cake (which should be in a coherent condition, but should not be fused) with water, and boil until the mass falls to powder, filter, precipitate with ammonium carbonate and ammonia, and proceed as in *a*.]

3. *Examination for fluorine, chlorine, boric acid, phosphoric acid, arsenious acid, arsenic acid, and sulphuric acid.*

For this purpose, use the portion of the fused mass 230
reserved in **227**, or, if necessary, fuse a separate portion of the finely pulverized substance with 4 parts of pure sodium-potassium carbonate until effervescence ceases, boil the mass with water, filter the solution, which contains all the fluorine as sodium or potassium fluoride, all the chlorine as sodium or potassium chloride, all the boric acid as borate, all the sulphuric acid as sulphate, all the arsenic and arsenious acid as arsenate and arsenite, and at least a part of the phosphoric acid as phosphate of sodium or potassium, and treat as follows:

a. Acidify a small portion with nitric acid, and test for CHLORINE with silver nitrate.

b. Test another portion for BORIC ACID, as directed in § 174, 5.

c. To detect FLUORINE, treat a third portion as directed in § 176, 7.

d. Acidify the remainder with hydrochloric acid, and test a small portion with barium chloride for SULPHURIC ACID; test all the rest with hydrogen sulphide, first cold, then at 70°, for arsenic (§ 157, 12). If no precipitate forms, evaporate the fluid (but if a precipitate forms, the filtrate) with addition of nitric acid, to dryness, treat the residue with nitric acid and water, and examine the solution for PHOSPHORIC ACID with solution of ammonium molybdate in nitric acid (§ 172, 10).

C. Silicates which are partially decomposed by Acids.

§ 244.

Most rocks are mixtures of several silicates, of which some are often decomposable by acids, while others are not. If such substances were analyzed by the same method as the absolutely insoluble silicates, the analyst would doubtless detect all the elements present, but the analysis would afford no satisfactory insight into the actual composition of the rock. 231

It is therefore advisable to examine separately those constituents which show a different deportment with acids. For this purpose, digest the very finely pulverized substance for some time with hydrochloric acid at a gentle heat, filter off a small portion of the solution, evaporate the remainder with the residue to dryness, heat the residue at 100° or scarcely above, with stirring, until no more or very little acid vapor is evolved, allow it to cool, moisten with hydrochloric acid, heat with water, and filter.

The filtrate contains the bases of that part of the mixed mineral which has been decomposed by hydrochloric acid, and this is to be examined as directed in **221**. Examine the portion first filtered off as directed in **222**, γ. Test portions of the original substance for other acids as directed in **222**, α and β, and **223**; and by **224** for the state of oxidation in which any iron found is present. Boil the residue (which, besides the silicic acid separated from the decomposed portion of the silicate, contains that part of the mixture which has resisted the action of hydrochloric acid) with an excess of solution of sodium carbonate, filter hot, and wash, first with hot solution of sodium carbonate, and, finally, thoroughly with boiling water. Treat the residuary, undecomposed part of the rock, thus freed from the admixed separated silicic acid, according to § 243. Acidify the alkaline filtrate with hydrochloric acid, evaporate to dryness, treat with hydrochloric acid and water, filter off the silicic acid, render the filtrate alkaline with am-

monia, and warm; the precipitate thus formed (if any) is to be treated with the separated silicic acid according to 221, in order to detect titanic acid. In cases where it is of no interest to effect the separation of the silicic acid of the part decomposed by acids, the troublesome treatment with sodium carbonate may be omitted, and the decomposition of the residue at once taken up.

III. Analysis of Natural Waters.

§ 245.

In the examination of natural waters, the analytical 232
process is simplified by the circumstance that we know from experience what substances are usually present. Now, although a quantitative analysis alone can properly inform us of the true character of a water, since the differences between waters are principally caused by the different proportions of the constituents, still a qualitative analysis may render very good service, especially if the analyst notes whether a reagent produces a faint or a distinctly marked turbidity, a slight or a copious precipitate; for these circumstances will enable him to make an approximate estimate of the relative proportions of the constituents.

The analysis of ordinary drinking-waters (water from wells, springs, small streams, rivers, etc.) is separated here from that of mineral waters (in which we may also include sea-water); for although no well-defined line can be drawn between the two classes, yet the analytical examination of the former is necessarily by far the simpler, as the number of substances to be looked for is much more limited.

A. Analysis of Ordinary Potable Waters (Spring-water. Well-water, River-water, etc.

§ 246.

We know from experience that the substances to be 233
considered in the analysis of such waters are the following:

a. **Metals**: potassium, sodium, ammonium, calcium, magnesium, iron.

b. ACIDS, etc.: sulphuric acid, phosphoric acid, silicic acid, carbonic acid, nitric acid, nitrous acid, chlorine.

c. ORGANIC MATTERS.

d. MECHANICALLY SUSPENDED SUBSTANCES: clay, etc.

Potable waters actually contain other constituents besides those enumerated here, as may be inferred from the origin and formation of springs, etc., and as has, moreover, been fully established by the results of analytical investigations;* but the quantity of such constituents is so trifling that they commonly escape detection where a few liters, and not hundreds of liters, of the water are subjected to the analytical process. The mode of their detection is therefore omitted here, and I refer in connection with it, and also in regard to the oxygen and nitrogen (which never fail to be present in fresh waters) to my "Introduction to Quantitative Chemical Analysis."

1. THE WATER UNDER INVESTIGATION IS CLEAR.

234 1. Boil 1,000 to 2,000 g of the carefully collected water in a genuine porcelain dish to one half. (Glass vessels are not to be recommended, as boiling water attacks them much more than those of porcelain.) This generally produces a precipitate. Pass the liquid through a perfectly clean filter (free from iron and lime) in such a way that the precipitate remains in the dish as far as possible, then, after having removed the filtrate, wash the precipitate well with small amounts of water, and examine both as follows:

a. Examination of the precipitate.

235 This contains those constituents of the water which were kept in solution through the agency of free carbonic acid, or, as the case may be, in the

* CHATIN (Journ. de Pharm. et de Chim. (3), **27**, 418) found iodine in all fresh-water plants, but not in land plants, a proof that the water of rivers, brooks, ponds, etc., contains traces, even though extremely minute, of metallic iodides. According to MARCHAND (Comp. Rend., **31**, 495), all natural waters contain iodine, bromine, and lithium. VAN ANKUM has demonstrated the presence of iodine in almost all the potable waters of Holland. Further, it may be affirmed with the same certainty that all, or at all events most, natural waters contain compounds of strontium, barium, fluorine, etc.

form of bicarbonates, viz., calcium carbonate, magnesium carbonate, ferric hydroxide (which precipitates upon boiling a solution containing ferrous bicarbonate, as do also ferric silicate, and, in presence of phosphoric acid, ferric phosphate); calcium phosphate; also silicic acid, and sometimes calcium sulphate (if that substance is present in large proportion).

Now pour a small amount of hot hydrochloric acid diluted with about three parts of water upon the precipitate on the filter, the point of which has been perforated by means of a platinum wire, and allow the resulting solution to flow into the dish which contains the greater part of the precipitate produced by boiling. An effervescence is usually observed in this operation, caused by the escape of CARBON DIOXIDE. Heat the dish somewhat, and proceed with the solution, which is often not quite clear, as follows:

α. To a portion add potassium sulphocyanide, 236
to test for IRON.*

β. Evaporate the whole of the remainder in a small porcelain dish to dryness upon the water-bath, moisten the residue with hydrochloric acid, warm, add water, and filter off the SILICIC ACID remaining undissolved. Evaporate a portion of the filtrate with nitric acid to a small volume, and test with molybdic acid solution for PHOSPHORIC ACID (§ 172, 10). Test another portion for SULPHURIC ACID, with barium chloride. To the remainder add ammonia until it is in excess, filter if necessary, mix the filtrate with ammonium oxalate in some excess, and allow it to stand for some time in a warm place. White precipitate: CALCIUM (carbonate, or also sulphate if sulphuric acid has been found in the hydrochloric acid solution of the precipitate

* That the test for iron may be decisive, it is necessary to be sure of the fact that the water has suffered no contamination from dust or anything of the kind during the evaporation. The safest plan is to evaporate to a small volume a separate portion of the water in a retort or flask, with the addition of a few drops of hydrochloric acid and a drop of nitric acid, and after cooling to test this with potassium sulphocyanide.

produced by boiling the water). Filter, mix the filtrate with more ammonia, add some sodium ammonium phosphate, stir gently with a glass rod, and let it stand for 12 hours. White, crystalline precipitate, which is sometimes to be seen attached to the glass, only after pouring off the liquid, MAGNESIUM (carbonate).*

b. Examination of the filtrate.

237 *α.* Mix a portion with a little hydrochloric acid and barium chloride. A white precipitate, which makes its appearance at once, or perhaps only after standing some time in a warm place, indicates SULPHURIC ACID.

β. Mix a portion with nitric acid and add silver nitrate. A white precipitate or turbidity indicates CHLORINE.

γ. Test a portion for PHOSPHORIC ACID by evaporating with nitric acid and adding molybdic acid solution to the nitric acid solution of the residue (§ 172, 10).

238 *δ.* Evaporate a larger portion until highly concentrated, and test the reaction of the fluid. If it is alkaline, if a drop of the concentrated clear solution effervesces when mixed on a watch-glass with a drop of acid, and if calcium carbonate precipitates on the cautious addition of calcium chloride to the alkaline fluid, then a CARBONATE of an ALKALI METAL is present. Evaporate the fluid to perfect dryness, boil the residue with alcohol, filter, evaporate the solution to dryness, dissolve the residue in a little water, and test the solution for NITRIC ACID,† as directed in § 193, 7, 8, 9, or 10.

* Very small amounts of magnesium are detected with more certainity if, before testing for it, the ammonium salts are volatilized, the residue dissolved in dilute hydrochloric acid, the solution mixed with ammonia, and sodium-ammonium phosphate is added.

† This somewhat long but exact process is frequently not necessary. The nitric acid is detected instead, without trouble, by directly testing the water, evaporated to a small volume. Well-waters often give the nitric acid reaction with diphenylamine or with brucine (§ 193, 10 and 8), without previous concentration.

ε. Evaporate all the rest of the liquid, with the addition of some hydrochloric acid, at last upon the water-bath, to dryness, moisten the residue with hydrochloric acid, warm, add water, filter off any SILICIC ACID remaining, make alkaline with ammonia, add ammonium oxalate, and let the liquid stand in a warm place for some time. A precipitate shows CALCIUM. Filter this off, and test 239

aa. A small portion with ammonia and sodium ammonium phosphate for MAGNESIUM.

bb. Evaporate the rest to dryness, ignite, separate any magnesium that may be present (168, *β*) and test according to 169 to 172 for POTASSIUM and SODIUM.

2. In order to test for AMMONIA,* add to a fresh portion of the water, about 300 cc, in a glass cylinder, in a room free from ammonia vapors, 2 cc of a saturated solution of sodium carbonate, and 1 cc of a solution of sodium hydroxide (1 part of sodium hydroxide in 2 parts of distilled water), stopper the cylinder, shake, and let the precipitate settle. Pour off or filter (through a washed filter) 100 cc of the clear liquid into another cylinder, and add 1 cc of the solution of potassium mercuric iodide in potassium hydroxide (NESSLER'S reagent), mentioned in § 97 *b*. If this produces a yellow coloration, or perhaps, upon the addition of another cubic centimeter of NESSLER'S reagent, even a reddish-brown turbidity, a smaller or larger quantity of ammonia is shown to be present. 240

3. In order to test for NITROUS ACID,* to a fresh portion of the water (about 50 cc) add about 1 cc of dilute sulphuric acid and 1 cc of potassium iodide or zinc iodide and starch solution (compare § 189). If a blue coloration appears at once, or after a very short time, there is a relatively large amount of nitrous acid present, but if the color appears only after a considerable time, a slight amount is present. In making the test, avoid the action of daylight, and especially that of direct sunlight, because otherwise a blue color appears, or may appear 241

* Compare also, in regard to this, the corresponding chapter of my "Quantitative Analysis."

even when nitrous acid is not present. In making this test, caution requires that a counter-experiment should be made with the same reagents and a water free from nitrous acid. If it is desired to increase the delicacy of the reaction still more, or if substances are present which interfere with direct testing according to the method given above, distil a larger portion of the water acidified with acetic acid, and subject to the test the portion which first comes over (compare § 189).

4. To test for ORGANIC MATTER, it generally suffices for the qualitative examination of a water to evaporate about 200 cc to dryness, and to subject the residue to a gradually increasing heat. Organic substances are then recognized by a browning or blackening. If the heating has not been carried too far, upon treating the residue, which usually contains carbonates, with dilute hydrochloric acid, carbonic acid with an empyreumatic odor is generally evolved. If this test is to give a decisive result, the evaporation, as well as the heating of the residue, must be performed in a glass flask or a retort.*

5. FETID SUBSTANCES (decaying organic matter) are 242
detected best by filling a bottle to two-thirds with the water, covering it with the hand, shaking, and smelling. If the smell is of hydrogen sulphide, proceed as directed in § 248, 3. Whether there are also fetid organic matters present, may be ascertained by adding a little copper sulphate to the water before smelling it.

6. Treat another sample of the freshly drawn water with lime-water. If a precipitate is produced, FREE CARBONIC ACID or ACID CARBONATES are present. In the first case, a permanent precipitate is not obtained if a large portion of the water is treated with but little lime-water,

* In relation to more exact tests for organic matters, compare the Sixth Edition of my "Anleitung zur Quantitativen Chemischen Analyse," § 205, 11. In regard to micro-bacteriological investigation, see HUEPPE, "Die Methoden der Bakterien-Forschung" Wiesbaden, C W. Kreidel's Verlag, 1885; v. MALAPERT NEUFVILLE, Zeitschr. f. analyt. Chem. **25**, 39; G. FRANK, *ibid*. **30**, 305; OHLMÜLLER, "Die Untersuchung des Wassers," Berlin, J. Springer's Verlag, 1894.

(because in this case a soluble acid calcium carbonate is formed).*

7. In order not to overlook LEAD, ZINC, or COPPER, which sometimes occur in waters from the use of lead, "galvanized," or copper service-pipes, acidify 1 or 2 litres of the water with hydrochloric acid, concentrate it in a tubulated retort, having the tubulure open and the neck directed steeply upwards, to a residue of about 100 cc, filter if necessary, and treat the liquid with hydrogen sulphide. Since a portion of the lead present might possibly be in the precipitate filtered off, heat this with a solution of ammonium acetate, filter, and test this filtrate with hydrogen sulphide for lead.

If a black precipitate was obtained by treating the first solution with hydrogen sulphide, examine it for lead and copper by § 229.

Boil the liquid which has been filtered from the black precipitate, or that in which such a precipitate has not been obtained, until the hydrogen sulphide has been expelled, add some nitric acid, boil again, mix, after cooling, with ammonia in excess, filter off any resulting precipitate (ferric hydroxide, etc.), just acidify the filtrate with acetic acid, and treat with hydrogen sulphide. If a white precipitate is produced which does not dissolve upon shaking with benzol or petroleum-ether, the presence of zinc is shown.

II. THE WATER UNDER INVESTIGATION IS NOT CLEAR.

1. Fill a large glass bottle with the water, stopper it, **243** and let it stand in a dark, cool place until clear, then draw off the clear water by means of a siphon, and apply to it the tests given in I, 1, 4, and 6.

2. To test for ammonia (I, 2), nitrous acid (I, 3), fetid organic matter (I, 5), and lead, zinc, and copper (I, 7), use fresh portions of the water in its original, turbid condition, and in this case, it is generally preferable to use the distillation method for testing for nitrous acid.

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* In regard to other methods of detecting free carbonic acid, see § 179, 8 and 9.

3. In order to learn the character of the suspended substances, filter the deposit left in the bottle in letting the water become clear (II, 1), and examine the precipitate remaining on the filter. Since it may consist of the finest dust of various minerals, treat it first with dilute hydrochloric acid, and examine the part insoluble in this acid by the course for silicates (§ 241).*

B. Analysis of Mineral Waters.

§ 247.

The analysis of mineral waters embraces a larger num- 244
ber of constituents than that of potable water. The following are the principal of the additional bodies to be looked for:

Cæsium, rubidium, thallium, lithium, barium, strontium, aluminium, manganese, boric acid, titanic acid, bromine, iodine, fluorine, hydrogen sulphide (thiosulphuric acid),† crenic acid, and apocrenic acid (formic acid, propionic acid, etc., nitrogen gas, oxygen gas, marsh gas).†

The analyst has, moreover, to examine the muddy, ocherous or hard sinter deposits of the spring, or also the residue left upon the evaporation of very large quantities of water, for arsenic, antimony, copper, lead, zinc, cobalt, nickel, and other heavy metals. The greatest care is required in this examination to be sure that these metals really come from the water, and do not perhaps proceed from pipes, stop-cocks, etc.‡ The absolute purity of the reagents employed in these delicate investigations must also be established with the greatest care.

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* In regard to a more exact examination, compare the corresponding chapter of my "Quantitative Analysis."

† Respecting the constituents in parentheses, I refer to the corresponding chapter in my "Quantitative Analysis," as the detection of these matters generally comprises also their quantitative estimation.

‡ In relation to this, and in regard to the analysis of mineral waters in general, compare my numerous analyses of mineral waters, given in the corresponding chapter of my "Quantitative Analysis."

1. Examination of the Water.

a. Operations at the Spring.

§ 248.

1. Filter the water, if not perfectly clear, through washed filter-paper (§ 5), into large bottles with glass stoppers. The sediment remaining on the filter, which, besides the flocculent matter suspended in the water, possibly contains also those constituents which separate at once upon coming in contact with the air (ferric hydroxide and ferric phosphate, silicate, and arsenate), is taken to the laboratory, to be afterwards examined according to § 250. 245

2. The presence of FREE CARBONIC ACID is usually sufficiently evident to the eye. However, to make sure by positive reactions, test the water with freshly prepared solution of litmus and with lime-water. If carbonic acid is present, the former acquires a wine-red color, while the latter produces a turbidity which must disappear upon addition of the mineral water in excess. 246

3. Free HYDROGEN SULPHIDE is most readily detected by the smell. For this purpose half fill a bottle with the mineral water, cover with the hand, shake, and then smell the air in the bottle. In this way distinct traces of hydrogen sulphide are often found which would escape detection by reagents. However, if visible reactions are desired, fill a large white bottle with the water, add a few drops of solution of lead acetate in sodium hydroxide, or, if a heavy white precipitate should be produced by this, an aqueous solution of cupric chloride, place the bottle on a white surface, and look in at the top, to see whether the water acquires a brownish color or deposits a blackish precipitate. Another test, also very delicate, depending upon the formation of methylene blue, is the following: Mix the water to be tested with $\frac{1}{50}$ of its volume of fuming hydrochloric acid, add a few crystals of the sulphuric acid salt of para-amido-dimethyl aniline, and, as soon as these have dissolved, one or two drops of a dilute solu- 247

tion of ferric chloride. In the presence of hydrogen sulphide, the liquid, which would otherwise be light red, assumes a pure blue color after some time (H. CARO, E. FISHER; see § 187, 6).

Both the browning by lead sulphide or copper sulphide and the formation of methylene blue take place whether hydrogen sulphide or an alkali-metal sulphide is present. Therefore, if the alkaline character of the water points to the possible presence of an alkali-metal sulphide, and if the odor of hydrogen sulphide cannot be distinctly recognized, the following experiment must be made for the detection of the latter: Close a large bottle, half filled with the water, with a cork, to the bottom of which a strip of paper impregnated with lead acetate solution and then moistened with a solution of ammonium carbonate is fastened, and notice whether this becomes brown in the course of several hours. Shake the bottle a little from time to time.

4. Mix a rather large sample of the water with some tannic acid, and another with some gallic acid. If the former imparts a reddish-violet, and the latter a bluish-violet, color, FERROUS COMPOUNDS are present. Instead of the two acids, infusion of galls, which contains them both, may be employed. The colorations make their appearance only after some time, and increase in intensity from the top (where the air acts on the fluid) towards the bottom of the vessel. Test for occasionally occurring *ferric salts* by means of potassium sulphocyanide, with the addition of hydrochloric acid. 248

5. Test for NITROUS ACID and FETID ORGANIC SUBSTANCES according to **241** and **242**. If the water contains hydrogen sulphide, remove it, before testing for nitrous acid, by the addition of some freshly precipitated, washed lead carbonate and filtering. 249

b. OPERATIONS IN THE LABORATORY.

§ 249.

As it is always desirable, even in a qualitative examination, to obtain some information as to the proportions in which the several constituents are present, it is

advisable to analyze a comparatively small portion for the principal constituents, and to ascertain, as far as may be practicable, the relative proportions in which these exist, and thus to determine the character of the water; then to examine a far larger portion for the constituents which are present in small quantity; and finally a very large portion, or else the sinter, for those which are present in exceedingly small amounts. For this purpose proceed as follows:

1. Examination for those Constituents which are present in large Quantities.

250 *a.* Boil about 1½ liters of the clear water, or of the water filtered at the spring, in a porcelain dish (a flask is less suitable) for one hour, taking care, however, to add from time to time some distilled water, so that the quantity of liquid may remain undiminished, and only those salts may be separated which owe their solution to the presence of carbonic acid. Filter and examine both the precipitate and the filtrate as directed in § 246.

b. Test also for ammonium, organic matters, etc., by the methods given in § 246. If from any cause, the water is not adapted for being tested directly for ammonia, according to **240**, distil it with the addition of some freshly boiled sodium or potassium hydroxide solution, and apply the test to the distillate. Attention is again explicitly called to the fact that the reaction for ammonia with Nessler's reagent does not occur when the liquid contains free carbonic acid, acid carbonates, or alkali-metal sulphates (compare § 97).

2. Examination for those fixed Constituents which are present in smaller Quantities.

251 Evaporate to dryness a large quantity (at least 10 liters) of the water, in a platinum, silver, or porcelain dish; conduct this operation with the most scrupulous cleanliness, in a place as free as possible from dust. If the water contains no alkali carbonate, add pure potassium carbon-

ate in slight excess. The first part of the process of evaporation may be conducted over a gas-lamp, but ultimately the sand-bath must be employed. Heat the dry mass to very faint redness; if in a platinum or silver dish, proceed to ignite it directly, but if in a porcelain dish, first transfer it to a silver or platinum vessel, and then ignite gently. If the mass turns black in this process, ORGANIC MATTERS may be assumed to be present.*

Mix the residue thoroughly, and divide it into 3 portions, *a* and *b* being each about a quarter, and *c* one half.

a. EXAMINATION FOR PHOSPHORIC ACID.

252 Warm the portion *a* with water, add pure hydrochloric acid in sufficient excess, evaporate to dryness on the water-bath, warm the residue with hydrochloric acid, dilute slightly, filter through paper washed with hydrochloric acid and water, evaporate the solution to a small volume, at last with repeated additions of nitric acid, and test with the nitric acid solution of ammonium molybdate, for PHOSPHORIC ACID (§ 172, 10).

b. EXAMINATION FOR FLUORINE.

253 Heat the portion *b* with water, add calcium chloride as long as a precipitate (consisting chiefly of calcium and magnesium carbonates) continues to form; let this settle, and collect it on a filter. Wash, dry, ignite, treat with water in a small dish, add acetic acid in slight excess, evaporate to dryness on the water-bath, keeping the dish on the bath until all smell of acetic acid has disappeared, add water, heat, filter off the solution of the acetates of the alkali-earth metals, wash, dry or ignite the residue, and test it for FLUORINE, as directed in § 176, 6.

c. EXAMINATION FOR THE REMAINING FIXED CONSTITUENTS PRESENT IN MINUTE QUANTITIES.

254 Boil the portion *c* repeatedly with water, filter,

* This inference, however, is correct only if the water has been effectually protected from dust during evaporation; if this has not been the case, and it is desired to ascertain beyond doubt whether organic matters are present, evaporate a separate portion of the water in a retort. If organic matter is found, in order to learn whether it consists of crenic acid or of apocrenic acid, treat a portion of the residue as directed in § 250, 3.

and wash the undissolved residue with boiling water. This gives a residue (α) and a solution (β).

α. The *residue* consists chiefly of calcium carbonate, magnesium carbonate, silicic acid, and (in the case of chalybeate springs) ferric hydroxide. But it may also contain minute quantities of BARIUM, STRONTIUM, ALUMINIUM, MANGANESE, and TITANIUM, and accordingly must be examined for these substances.

Treat it with water in a platinum or porcelain dish, add hydrochloric acid in slight excess, then 4 or 5 drops of dilute sulphuric acid, evaporate to dryness on the water-bath, moisten with a small quantity of hydrochloric acid, then add water, warm gently, filter, and wash.

aa. EXAMINATION OF THE RESIDUE INSOLUBLE IN HYDROCHLORIC ACID. This will consist mostly of silicic acid; but it may also contain sulphates of the alkali-earth metals, titanic acid, and carbon. Heat it repeatedly in a platinum dish with hydrofluoric acid or ammonium fluoride, with addition of some sulphuric acid, till all the silicic acid is expelled. Finally evaporate to dryness, fuse the residue (if any) with potassium disulphate, treat the fusion with cold water, filter, and test the solution for TITANIC ACID by protracted boiling. If, on treating the fusion with water, there was a residue, wash it, and incinerate the filter. When a spectroscope is at hand, take up the ash on the loop of a platinum wire, expose for some time to the reducing flame, moisten with hydrochloric acid, and examine for BARIUM. Strontium will not be found here except perhaps in traces. When a spectroscope is not at hand, set aside the ash for subsequent examination. 255

bb. EXAMINATION OF THE HYDROCHLORIC ACID SOLUTION. Mix it in a flask with some ammonium chloride, add ammonia until the fluid is just alkaline, then some freshly prepared ammonium sulphide which is free from ammonium hydrox- 256

ide; close the flask, filled to the neck, and let it stand for 24 hours in a moderately warm place. If a precipitate has formed at the end of that time, filter it off, dissolve in hydrochloric acid, boil, add sodium hydroxide (§ 35, *c*) in excess, boil again, filter, and test half of the filtrate for ALUMINIUM,* by adding ammonium chloride; and the other half for ZINC, by adding a little hydrogen sulphide water. Fuse a part of the residue with sodium carbonate to test for MANGANESE, and test the remainder for IRON by dissolving it in hydrochloric acid, boiling the solution with a little nitric acid, and adding potassium sulphocyanide or ferrocyanide to the cooled and diluted liquid.

If the examination of the precipitate obtained by ammonium sulphide is to be extended only to manganese and zinc, it is preferable, in the presence of much iron, to oxidize the solution of the precipitate in hydrochloric acid, by boiling with nitric acid, to precipitate the iron as a basic salt by § 128, 3, *b*, to add sodium acetate to the filtrate and acidify it with acetic acid, and to precipitate with hydrogen sulphide any zinc present; then test for manganese in the filtrate with bromine and ammonia (§ 128, 4).

The filtrate from the ammonium sulphide precipitate may contain traces of manganese and barium, and will contain all or nearly all the strontium. Acidify it first with hydrochloric acid, concentrate by evaporation, filter off the separated sulphur, add bromine-water until a strong yellow coloration is produced, then ammonia in slight excess, and heat to boiling for some time. If a minute, brown precipitate separates here, it is due to traces of manganese which had not been precipitated by ammonium

* When aluminium is found, one is not justified in supposing it to be present in the water unless the evaporation, etc., has been carried out in platinum or silver, rather than in porcelain.

sulphide. Filter, if the case requires it, precipitate with ammonium carbonate with the addition of ammonia, filter after long standing, wash the precipitate, dry it, subject it to ENGELBACH'S process (described near the end of § 104), and then treat the aqueous extract of the ignited precipitate as follows: If a spectroscope is at command, evaporate the extract to dryness with hydrochloric acid, and, by means of that instrument, examine the residue for STRONTIUM and any BARIUM that may be present here. If a spectroscope is not at hand, evaporate the aqueous extract nearly to dryness, with the addition of some ammonium sulphate, boil with a saturated solution of ammonium sulphate, filter, wash the precipitate, dry, incinerate, add the residue set aside in 225, fuse with sodium carbonate, treat with water, wash, dissolve the residue in nitric acid, evaporate to dryness, and proceed with the nitrates according to 163, in order to test for BARIUM and STRONTIUM.

257 *β.* The *alkaline solution* contains the salts of the alkali metals, and usually also magnesium and traces of calcium. It is to be examined for NITRIC ACID,* BORIC ACID, IODINE, BROMINE, and LITHIUM. Evaporate until *very* concentrated, let it cool, and place the dish in a slanting position, so that the small quantity of liquid may separate from the saline mass; transfer a few drops of the concentrated solution to a watch-glass by means of a glass rod, just acidify with hydrochloric acid, and test with turmeric-paper, for BORIC ACID (§ 174, 5). Evaporate the whole contents of the dish to perfect dryness, with stirring, and divide the residuary powder into two portions, *aa* being about two thirds, and *bb* one third.

* The nitric acid originally present may have been destroyed by the ignition of the residue in 251, if the latter contained organic matter. If there is reason to fear that such has been the case, and nitric acid has not been already found in 250, examine a larger portion of the non-ignited residue for that acid, according to 258.

aa. EXAMINE THE LARGER PORTION FOR NITRIC ACID, IODINE, AND BROMINE. Put the powdered substance into a flask, add alcohol of 90 per cent, boil on the water-bath, and filter hot; repeat the operation a second and third time. Mix the alcoholic extract with a few drops of potassium hydroxide, distil off almost all the alcohol, and allow the residue to cool. If minute crystals separate, these may consist of potassium nitrate; pour off the fluid, wash the crystals with some alcohol, dissolve them in a very little water, and test the solution for NITRIC ACID with diphenylamine, indigo, or brucin (§ 193). Now evaporate the alcoholic solution quite to dryness. If nitric acid has not yet been found, dissolve a small portion of the residue in a very little water, and examine the solution for that acid. Treat the remainder or, as the case may be, the whole of the residue three times with warm alcohol, filter, evaporate the filtrate to dryness with the addition of a drop of potassium hydroxide solution, dissolve the residue in a very little water, acidify slightly with sulphuric acid, add some pure carbon disulphide, and finally test for IODINE with a drop of a solution of nitrous acid in sulphuric acid or very little of a solution of potassium nitrite. After shaking the mixture, and carefully observing whether the carbon disulphide shows a violet or reddish coloration (establishing the presence of IODINE), test the same liquid for BROMINE by the cautious addition of chlorine-water, according to the process given in § 188. 258

bb. EXAMINE THE SMALLER PORTION FOR LITHIUM. Warm the smaller portion of the residue (which, if lithium is present, must contain that metal as carbonate or phosphate) with water, add hydrochloric acid to distinctly acid reaction, evaporate *nearly* to dryness, then mix with 259

pure alcohol of 90 per cent, which will separate the greater portion of the sodium and potassium compounds, and dissolve all the lithium salt. Filter, drive off the alcohol by evaporation, and, if a spectroscope is at hand, examine the residue with this, for LITHIUM (§ 98, 3); but if not, dissolve the residue in water and a few drops of hydrochloric acid, add a little ferric chloride and enough milk of lime to give a strong alkaline reaction to the liquid, boil, filter, precipitate with ammonium oxalate, filter the solution (now freed from phosphoric acid and alkali-earth metals), evaporate it to dryness, and gently ignite until the ammonium salts are expelled; after the addition of a drop of hydrochloric acid, treat the residue with a mixture of absolute alcohol and anhydrous ether, filter the solution, concentrate it by evaporation, and finally ignite the alcohol. If it burns with a carmine-red flame, LITHIUM is present. For confirmation, convert it into lithium phosphate; but before deciding that a residue (obtained by evaporating with sodium phosphate and a little sodium hydroxide and treating with ammonia and water) is certainly lithium phosphate, it is always to be examined to ascertain whether it shows the characteristic properties of this compound (§ 98, 3).

3. EXAMINATION FOR THOSE CONSTITUENTS WHICH ARE PRESENT IN EXCEEDINGLY MINUTE QUANTITIES.

Evaporate 100 or 150 liters of the water by degrees, in 260
a large porcelain dish, or even in a large, perfectly clean iron vessel, until the salts soluble in water begin to separate. If the mineral water contains no sodium carbonate, add enough of that substance to render the liquid distinctly alkaline. After evaporation, filter the solution off, wash the precipitate without adding the washings to the first filtrate, and

a. Examine the *precipitate*, by the method given in § 250 for sinter deposits.

b. Mix the *solution* with hydrochloric acid to acid reaction, heat, precipitate with hydrogen sulphide the acids of arsenic possibly present here (262), and exactly precipitate with barium chloride the sulphuric acid which may be present, filter, evaporate the filtrate to dryness, digest the residue with alcohol of 90 per cent, and examine the solution for CÆSIUM and RUBIDIUM, according to § 98, near the end. Treat the residue insoluble in alcohol as follows: Make a hot, concentrated solution of it in water, add ammonia just in excess, and filter if necessary. To the solution which has remained clear, or to the filtrate containing but little free ammonia, add potassium iodide while it is hot. If a precipitate forms at once, or after long standing, filter it off, and test it for THALLIUM by means of the spectroscope (§ 130).

2. Examination of Sinter Deposits.

§ 250.

1. Free the deposit from impurities by picking, sifting, elutriation, etc., and from the soluble salts adhering to it by washing with water. Digest a large quantity (from 50 to 200 g) with water and hydrochloric acid (effervescence shows CARBONIC ACID) at a very moderate heat, until the soluble part is completely dissolved; then dilute, cool, filter, and wash the residue. 261

a. Examination of the filtrate.

α. Largely dilute a sample of it, neutralize the greater part of the free acid with ammonia, and, while still completely clear, mix the liquid with barium chloride, and allow it to stand for 12 hours in a warm place. White precipitate: SULPHURIC ACID.

β. Heat the larger portion to 70°, pass in hy- 262
drogen sulphide for a long time and also during the cooling. Allow it to stand in a moderately warm place till the smell of the gas is almost gone, and then pour it through a filter. IF THE PRECIPITATE CONTAINS A CONSIDERABLE AMOUNT OF SULPHUR (as is the case if the solution contained much ferric chloride), wash it completely by decantation, passing the washings through the filter, and while still moist, triturate it with water. Then wash the semi-liquid mass into a flask, add petroleum-ether, agitate thoroughly and persistently, pour off the liquid as far as possible into another flask, and repeat the extraction of the undissolved residue with water and petroleum-ether until the sulphur is completely or almost completely removed. If a residue remains undissolved (which indicates the presence of sulphides) filter the united liquids through a paper moistened with water, transfer the precipitate to it also, allow the water to run off entirely, then pour off the petroleum-ether from the sulphides adhering to the filter, spread out the moist filter in a small porcelain dish, and treat it according to **263**.

IF THE PRECIPITATE PRODUCED BY HYDROGEN SULPHIDE CONTAINS LITTLE SULPHUR, the treatment with petroleum-ether is not required. In this case, directly spread out the filter containing the well-washed precipitate, in a small porcelain dish. Warm the contents of the filter with some sodium 263
sulphide solution, dilute, filter, and wash with water containing some sodium sulphide. Distinctly acidify with hydrochloric acid the solution thus obtained, and shake thoroughly with petroleum-ether. If an insoluble residue remains, filter through a small paper moistened with water, allow the aqueous solution to run off entirely, pour off the petroleum-ether, wash the precipitate adhering to the paper, spread out the filter, first upon blotting-paper, then in a small porcelain dish, and proceed to examine for the metals of Group VI,

especially arsenic and antimony, according to § 157, 2, or some other method given in § 157.

If a residue remained on treating the hydrogen sulphide precipitate with sodium sulphide, wash, remove from the filter by a jet of water, and boil with a small quantity of dilute nitric acid. If a residue still remains, filter it off, and in order not to overlook any lead sulphate possibly present here, repeatedly pour over the contents of the filter a hot solution of ammonium acetate. Now test this filtrate with hydrogen sulphide for lead, and test the contents of the filter, if any should remain, for BARIUM and STRONTIUM, according to p. 163. Mix the nitric acid solution with pure sulphuric acid, evaporate to dryness upon the water-bath, and proceed to test for LEAD, COPPER, and any other metals of Group V that may be present, according to 132. 264

Take a portion of the filtrate from the hydrogen sulphide precipitate, evaporate it to dryness on a water-bath, with an excess of nitric acid, treat with nitric acid and water, filter, and test the solution for PHOSPHORIC ACID with molybdic acid solution. 265

Heat the remainder of the liquid which was filtered from the hydrogen sulphide precipitate, with the addition of nitric acid, until the ferrous chloride (which is almost always present, and often in large amount) is completely converted into ferric chloride, and then proceed, according as the solution contains little or much iron, by *aa* or *bb*.

aa. THE SOLUTION CONTAINS LITTLE IRON.

Mix it with ammonia in slight excess, filter, wash the precipitate somewhat, dissolve it in hydrochloric acid, heat to boiling, allow to cool, precipitate once more with a slight excess of ammonia, and filter again.

Dry the PRECIPITATE, triturate it, and having placed it in a porcelain boat within a glass tube, ignite it in a stream of hydrogen for some time, strongly enough to convert the ferric oxide present into metallic iron; let

it cool completely in hydrogen, and treat the residue with dilute nitric acid until the iron present is dissolved. If a residue remains, fuse it, after it has been washed, with potassium disulphate, treat the mass with cold water, filter off the undissolved SILICIC ACID which always remains, boil the filtrate for a long time, thus separating any TITANIC ACID present (§ 118), and test the solution, filtered from this, for ALUMINIUM by warming with ammonia in moderate excess. If a precipitate thus resulting should not be white but brownish-red (therefore still containing iron), it should be filtered off and washed, dissolved in hydrochloric acid, the solution then heated with an excess of potassium hydroxide, diluted, filtered, and the filtrate tested for aluminium by heating with ammonium chloride.

Acidify the SOLUTION with acetic acid, mix ammonium acetate with it, and while hot treat it with hydrogen sulphide gas. If a pure white precipitate is formed, which does not dissolve upon shaking with petroleum-ether, it shows the presence of ZINC; but if a black or blackish precipitate forms, this is to be tested for COBALT, NICKEL, and ZINC, according to **143**.

From the liquid which has been filtered from the precipitate produced by hydrogen sulphide in acetic acid solution, precipitate the almost never-failing manganese with bromine and ammonia (§ 123, 7), and test the liquid filtered from the hydrated manganese dioxide, for BARIUM, STRONTIUM, CALCIUM, and MAGNESIUM, according to **166** and **167**. If all of them should not be found here, dissolve the precipitate of hydrated manganese dioxide (which may contain small amounts of alkali earths) in hydrochloric acid with the aid of heat, precipitate the manganese with ammonia and ammonium sulphide, filter, and test this filtrate also for the alkali-earth metals, according to **166** and **167**.

bb. THE SOLUTION CONTAINS MUCH IRON.

Proceed in this case to precipitate the iron as basic chloride, according to § 128, 3, *b*, filter, wash with water containing ammonium chloride, concentrate the filtrate in a platinum dish, allow it to cool, then add ammonia in slight excess, filter, wash, unite this precipitate with the principal one first obtained, and proceed with this, and with the filtrate from the precipitation with ammonia, according to *aa*.

b. EXAMINATION OF THE RESIDUE.

This generally consists of sand, hydrated silicic acid, clay, and organic matters, but if the water contain hydrogen sulphide, the residue may contain sulphur besides barium sulphate, strontium sulphate, and calcium sulphate. First boil it for a long time with a solution of sodium carbonate and hydroxide, in order to dissolve the hydrated silicic acid and any sulphur present; then after diluting it, pour off the solution through a filter, boil the residue twice more with fresh sodium carbonate solution, bring the precipitate upon the filter, and wash it. 266

α. Examination of the Solution.

Acidify with hydrochloric acid a part of the filtrate first obtained (an odor of hydrogen sulphide shows the presence of SULPHUR in the deposit of the spring), evaporate to dryness, warm the residue with hydrochloric acid, add water, filter, wash, dry, and ignite the insoluble residue in order to free the SILICIC ACID which may be present, from any sulphur. If there is doubt about the presence of an alkali-metal sulphide in the alkaline solution, test a sample of it with alkaline lead solution (§ 187, 4).

β. Examination of the residue.

Treat the residue with dilute nitric acid, in order to dissolve any barium and strontium carbonates resulting from the conversion into carbonates (by boiling with sodium carbonate) of any sulphates of these metals originally present in the sinter. Test

the nitric acid solution for BARIUM and STRONTIUM, and examine the residue insoluble in nitric acid, according to § 243.

2. It is best to test a separate portion of the deposit for FLUORINE. If it does not already contain much calcium carbonate, mix it with about half its weight of pure calcium hydroxide, ignite (whereupon there is an opportunity to detect organic matter), mix the residue with water, add acetic acid to acid reaction, evaporate until all the acetic acid is driven off, and proceed according to **253**. **267**

3. Boil a portion of the deposit for a considerable time with concentrated potassium or sodium hydroxide solution, and filter. **268**

a. Acidify a portion of the filtrate with acetic acid, add ammonia, allow it to stand 12 hours, and then filter off the precipitate of alumina and silicic acid, which usually forms; again add acetic acid to acid reaction, and then solution of normal cupric acetate. If a brownish precipitate is formed, this consists of cupric APOCRENATE. Mix the fluid, filtered from the precipitate, with ammonium carbonate, until the green color has changed to blue, and then warm. If a bluish-green precipitate is produced, this consists of cupric CRENATE.

b. If arsenic has been detected, use the remainder of the alkaline fluid to ascertain whether it existed in the deposit as ARSENIOUS ACID or as ARSENIC ACID. (Compare § 157, 12.)

IV. Analysis of Cultivated or Natural Soils.

§ 251.

Soils must contain all the constituents which are found in the plants growing upon them, with the exception of those supplied by the atmosphere and the rain. When we find, therefore, a plant, the constituents of which are known, growing in a certain soil, the mere fact of its growing there gives us some insight into the composition

of that soil, and to some extent may save the trouble of a qualitative analysis.

Viewed in this light, it would appear superfluous to make a qualitative analysis of soils still capable of producing plants; for it is well known that the ashes of plants almost invariably contain the same constituents, and that the differences between them are caused principally by differences in the relative proportions in which the several constituents are present. But if, in the qualitative analysis of a soil, regard is also had to the proportions of the constituents, as far as it is possible to estimate them, and to the state in which they are present, an analysis of this kind, if combined with an examination of the physical properties of the soil and a mechanical separation of its parts,* may give useful results, enabling the analyst to judge sufficiently of the condition of the soil without the necessity of making a quantitative analysis, which would require much time, and is a far more difficult task.

As plants can only absorb substances capable of entering into a state of solution, it is a matter of special importance, in the qualitative analysis of a soil, to know which constituents are soluble in pure water; † which

* With regard to the mechanical separation of the component parts of a soil, and the examination of its physical properties, and chemical and bacteriological condition, compare the corresponding section of my "Quantitative Analysis," and the works and articles referred to there; also, N. PELLEGRINI, Landwirthschaftl. Versuchsstationen, **25**, 48; F. SESTINI, *ibid.*, **25**, 47; C. FRÄNKEL, Zeitschr. f. analyt. Chem., **27**, 104; "Bericht über Untersuchung der Bodenarten," *ibid.*, **30**, 225; F. WAHNSCHAFFE, "Anleit. zur wissenschaftlichen Bodenuntersuchung," Berlin, bei S. Parey, 1887, p. 20 *et seq.*; R. HEINRICH "Zweiter Bericht über die landswirthschaftl. Versuchsstation zu Rostock," p. 19 *et seq.*

† Formerly it was universally assumed that substances soluble in water, or in water containing carbonic acid, circulated freely in the soil so long as there existed agents for their solution; but since it has been discovered that arable soil possesses, like charcoal, the property of withdrawing from dilute solutions the bodies dissolved in them, this notion is exploded, and we now know that arable soil will retain with a certain force, bodies otherwise soluble; from which we conclude that the aqueous extract of a soil cannot be expected to contain the whole of the substances present in that soil in a state immediately available for the plant. Neither can we expect to find these matters in the aqueous extract in the same proportion in which they are present in the soil,

require an acid for their solution (in nature principally carbonic acid); and finally, which are neither soluble in water nor in acids, and accordingly, are not in a condition, for the time being, to afford nutriment to the plant. With regard to the insoluble substances, other interesting questions are—whether they suffer disintegration readily, or slowly and with difficulty, or whether they altogether resist the action of disintegrating agencies; and also what are the products which they yield upon their disintegration.

In order to take these matters into consideration in the analysis of soils, the constituents soluble in water, those soluble in acids, and the insoluble part, must be examined separately. The examination for organic substances also demands a separate process.

The analysis is therefore divided into the following four parts:

1. *Preparation and Examination of the Aqueous Extract.*

§ 252.

About 1000 g of the air-dried soil are used for the prep- 269
aration of the aqueous extract. To prepare this extract quite clear is a matter of some difficulty; in following the usual course (viz., digesting or boiling the earth with water, and filtering), the fine particles of clay are speedily found to impede the operation, by choking the pores of the filter. They also almost invariably render the filtrate turbid, at least the portion which passes through first. The following method, proposed by F. SCHULZE, accomplishes the purpose simply, and with comparative rapidity:* Close the neck of several middle-sized funnels

since the latter will readily give up to water those substances in regard to which its power of absorption has been satisfied, while it will more or less strongly retain others. But although the examination of the aqueous extract of a soil has no longer the same value as it was formerly considered to have, yet it is still useful to ascertain what substances a soil will actually give up to water. It is for this reason, therefore, that I have retained the chapter on the preparation and examination of the aqueous extract.

* In regard to other methods of preparing an aqueous extract, compare the corresponding section of my "Quantitative Analysis."

with small filters of thick filter-paper, moisten the filters, press them close to the sides of the funnels, place upon them layers of fine, pure sand 2 or 3 cm deep, and then introduce the air-dried soil (best in small lumps ranging from the size of a pea to that of a walnut, but not pulverized or even crushed), filling the funnels about two thirds. Pour distilled water into them, in sufficient quantity to cover the soil; if the first portion of the filtrate is turbid, pour it back into the funnel. Let the operation proceed quietly. Fill the funnels again with water, and continue this process of lixiviation until the filtrates weigh twice or three times as much as the soil used. Collect the several filtrates, which are often somewhat turbid, in a single vessel, and mix them thoroughly. Keep a portion of the soil which has been extracted as far as possible.

Divide the aqueous solution into two parts, 1 (about two thirds) and 2 (about one third).

1. Evaporate the two thirds in a porcelain dish to a small bulk, and test as follows:

a. Filter off a portion, test the reaction of the filtrate, set aside a part to test for organic matter (**280**), warm the rest and add nitric acid. Effervescence indicates an ALKALI-METAL CARBONATE. Then test half of this for CHLORINE with silver nitrate, the other half for SULPHURIC ACID with barium chloride. **270**

b. Transfer the rest of the concentrated fluid from 1, together with the precipitate which it usually contains, to a small dish of porcelain or, better, of platinum, evaporate to dryness, and heat the brownish residue cautiously over the lamp till the organic matter is destroyed. In the presence of NITRATES, a deflagration of greater or less intensity will be perceptible, according to the amount present. Treat the residue as follows: **271**

α. Test a small portion with sodium carbonate in the oxidizing flame, for MANGANESE (§ 123, 14).

β. Warm the rest with water, add some hydrochloric acid (effervescence indicates CARBONIC ACID), evaporate to dryness to separate silicic acid,

moisten with hydrochloric acid, add water, warm, and filter.

aa. Wash the residue, which generally contains a little carbon, a little clay (if the aqueous extract was not quite clear), and also SILICIC ACID. To detect the latter, pierce the filter, wash the residue through, boil it with a solution of sodium carbonate, filter, saturate with hydrochloric acid, evaporate to dryness, and finally take up with hydrochloric acid and water, when the silicic acid will remain behind.

bb. Test a part of the hydrochloric acid solution (after evaporating with the addition of nitric acid) for PHOSPHORIC ACID, with molybdic acid solution. Test a second part for IRON with potassium sulphocyanide. To the rest add a few drops of ferric chloride (to remove phosphoric acid), then ammonia carefully till slightly alkaline, warm a little, filter, throw down the CALCIUM with ammonium oxalate, and proceed to the examination for MAGNESIUM, POTASSIUM, and SODIUM exactly according to the usual course of analysis (§§ 232 and 233). Finally examine a small quantity of the pure alkali-metal chlorides in the spectroscope, for LITHIUM.

Aluminium is not likely to be found in the clear aqueous extract (F. SCHULZE never found it). To test for it, boil the precipitate produced by ammonia with pure potassium hydroxide in a platinum or silver dish, dilute, filter, acidify the filtrate with hydrochloric acid, add ammonia, and warm. 272

2. If iron has been found, acidify a portion of the one third of the aqueous solution with hydrochloric acid, and test half with potassium ferricyanide, and the other half with potassium sulphocyanide, to ascertain in what state the iron is present. Test the rest of the aqueous extract for NITRIC ACID, AMMONIA, and NITROUS ACID, according to § 193, 7, 8, or 10, 240 and 241. 273

2. *Preparation and Examination of the Acid Extract.*

§ 253.

Heat about 50 g of the soil from which the part soluble in water has been removed as far as practicable (it is usually impossible to effect a complete extraction) with moderately strong hydrochloric acid (effervescence indicates CARBONIC ACID) for several hours on the water-bath, filter, and make the following experiments with the filtrate, which is generally yellow from the presence of ferric chloride: 274

1. Test a small portion with potassium sulphocyanide for FERRIC IRON, another with potassium ferricyanide for FERROUS IRON.

2. Evaporate a portion to dryness, heat the residue to a temperature scarcely exceeding 100°, moisten with hydrochloric acid, add some water, warm, add more water, and filter off the silicic acid, which is generally colored by organic matter, but becomes white upon ignition in the air. Test a part of the filtrate with barium chloride for SULPHURIC ACID, and, with repeated addition of nitric acid, evaporate the rest to a small residue, and test this for PHOSPHORIC ACID, with solution of ammonium molybdate in nitric acid. 275

3. Use a larger portion for the detection of MANGANESE, ALUMINIUM, CALCIUM, MAGNESIUM, POTASSIUM, and SODIUM, according to the usual course, proceeding with it according to **134** and what follows, in case only a slight amount of organic matter has gone into the hydrochloric acid solution; but, in the opposite case, according to **161**. 276

4. If it is of interest to determine whether the hydrochloric acid extract contains ARSENIC ACID, COPPER, etc., treat the remainder of the solution with hydrogen sulphide, etc., as directed in **262** to **264**. 277

5. It is best to test for fluorine (in case this test is required) in a new portion of the ignited earth, according to **230**.

3. *Examination of the Inorganic Constituents Insoluble in Water and Acids.*

§ 254.

Heating the soil with hydrochloric acid (274) always 278
leaves the greater portion undissolved. To subject this residue to chemical examination, wash, dry, and sift, to separate the coarser stones and gravel from the clay and sand; moreover, separate the two latter substances from each other by elutriation. Subject the several portions to the process given for silicates (§ 241).

4. *Examination of the Organic Constituents of the Soil.*

§ 255.

The organic constituents of the soil, which exercise 279
so great an influence upon its fertility, both by their physical and chemical action, are partly portions of plants in which the structure may still be recognized (fragments of straw, roots, seeds of weeds, etc.), and partly products of decay which are usually called by the general name of HUMUS. The latter differ in their constituents and properties, according to whether they result from the decay of the nitrogenous or non-nitrogenous substances, whether alkalies or alkali earths have or have not had a share in their formation, and whether they are in the incipient or in a more advanced stage of decomposition. To separate the several component parts of humus (which are as yet by no means thoroughly investigated nor sharply characterized) would be an exceedingly difficult task, and the results would hardly repay the trouble. The following operations are amply sufficient to answer all the purposes of a qualitative analysis:

a. Examination of the Organic Substances soluble in Water.

Evaporate the portion reserved in 270 to perfect dry- 280
ness on the water-bath, and treat the residue with water.

The ulmic, humic, and geic acids, which were present in the solution in combination with bases, remain undissolved, while CRENIC and APOCRENIC ACIDS are dissolved in combination with ammonium (BERZELIUS). For the manner of detecting the latter acids, see 268.

b. Treatment with Alkali-metal Carbonate.

281 Dry a portion of the soil which has been extracted with water, and sift, in order to separate the fragments of straw, roots, the small stones, etc., from the finer parts; digest the latter for several hours at 80° or 90° with solution of sodium carbonate, and filter. Mix the filtrate with hydrochloric acid to acid reaction. If brown flakes separate, these proceed from ULMIC, HUMIC, or GEIC ACIDS. With more ulmic acid, the precipitate is lighter brown, while with more humic or geic acid, it is darker brown.

c. Treatment with Caustic Alkali.

282 Wash the soil boiled with solution of sodium carbonate (*b*) with water, boil several hours with potassium hydroxide solution (replacing the water as it evaporates), dilute, filter, and wash. Treat the brown fluid as in *b*. The acids of humus which separate here are new products (ulmic and humic acids), resulting from the action of boiling caustic potash upon ULMIN and HUMIN.

V. DETECTION OF INORGANIC SUBSTANCES IN PRESENCE OF ORGANIC SUBSTANCES.

§ 256.

It will be readily perceived that the presence of organic substances may so far impede an analysis that it cannot be proceeded with until the organic matter has been totally destroyed. For instance, the presence of organic coloring matter may completely conceal a change of color or a precipitate; again, the presence of slimy matter may render filtration impossible. Difficulties of

this kind are of constant occurrence in the examination of medicines, in the analysis of articles of food or of the contents of a stomach for inorganic poisons, and in the analysis of the inorganic constituents of vegetable or animal substances. In the following pages, instructions will be given first for a general procedure, afterwards for several special cases.

1. *General Rules for the detection of Inorganic Substances in the Presence of Organic Matters, which, by their Color, Consistence, or other Properties, impede the Application of the Reagents, or obscure the Reactions produced.*

§ 257.

We confine ourselves here, of course, to a description of the most generally applicable methods, leaving the modifications which circumstances may require in special cases to the discretion of the analyst.

1. THE SUBSTANCE DISSOLVES IN WATER, BUT THE SOLUTION IS DARK COLORED OR OF SLIMY CONSISTENCE.

283 *a.* Heat a portion of the solution with hydrochloric acid on the water-bath, and gradually add potassium chlorate until the mixture is decolorized and perfectly fluid; heat until it no longer exhales the odor of chlorine, then dilute with water, cool, and filter. Examine the filtrate in the usual way, commencing at § 226. (Compare also § 262.) It is hardly necessary to mention that mercurous, stannous, and ferrous salts would be changed to mercuric, stannic, and ferric chlorides, respectively, by this treatment, and that the original state of oxidation of such metals would not be shown in the examination of this solution. When mercury is especially sought for, it must be remembered that, when the foregoing process is followed, a part of this metal may remain undissolved in combination with albuminoids. In order to overcome this difficulty, LUDWIG recommends boiling at first for several hours with hydrochloric acid, in a flask connected with a return condenser, in order

to break up this compound, and afterwards to proceed with the treatment with potassium chlorate.

b. Boil another portion of the solution for some time with nitric acid, filter, and test the filtrate for SILVER and POTASSIUM. If nitric acid succeeds in effecting the ready and complete destruction of the coloring and slimy matters, etc., this method is often preferable to all others.

c. ALUMINIUM and CHROMIUM might escape detection by this method, because ammonia and ammonium sulphide fail to precipitate their hydroxides from fluids containing non-volatile organic substances. If there is reason for considering these metals, mix a third portion of the substance with sodium carbonate and sodium peroxide or potassium chlorate, and introduce the mixture in portions into a red-hot crucible. Let the mass cool, then treat it with water, and examine the solution for chromic acid and aluminium, and the residue for aluminium (§ 108).

d. Test a separate portion for AMMONIA with slaked lime.

e. Subject another portion to dialysis (§ 8), and examine the diffused part for acids, and, if the case requires it, for the state of oxidation of the metals present.

2. BOILING WATER FAILS TO DISSOLVE THE SUBSTANCE, OR EFFECTS ONLY PARTIAL SOLUTION; THE LIQUID ADMITS OF FILTRATION. 284

Filter, and treat the filtrate either as directed in § 225, or, should it require decoloration, according to 283. The residue may vary in character.

a. It is FATTY or RESINOUS. Remove the fatty or resinous matter by means of ether, petroleum-ether, carbon disulphide, or some other appropriate solvent (if possible, one that does not mix with water), shake the liquids, separated from any insoluble residue, first with water, then again with water acidified with hydrochloric or nitric acid, and examine the solutions thus obtained by the usual course of analysis. If a residue remains after treatment with ether

or one of the other solvents mentioned, examine it according to *b*.

b. IT IS OF A DIFFERENT NATURE, *e.g.*, woody fiber, etc.

α. In the first place, endeavor to extract any substances which are soluble in acids, by means of hydrochloric acid, nitric acid, or aqua regia, and use this solution (which may be decolorized, if necessary, by passing in chlorine, or heating with bromine or potassium chlorate) for the detection of metals and acids according to the usual course. If a residue remains which is insoluble even in aqua regia, wash it with water, and if the presence of sulphur is suspected, dry it and warm it with petroleum-ether or carbon disulphide, and filter. Carefully incinerate the residue thus left, and test it by § 239.

β. In order to test for metals whose compounds do not volatilize at a moderate red heat, or which are not volatilized by the action of carbon upon their compounds at such a temperature,* a portion of the residue insoluble in water may be heated to partial or complete incineration in a porcelain or platinum vessel, avoiding too high a temperature. Then warm the residue with hydrochloric acid and a little nitric acid, dilute with water, and examine the solution according to § 226, but any residue by § 239.

γ. Test another portion of the residue for ammonia, by triturating it with calcium hydroxide and a little water.

3. THE SUBSTANCE DOES NOT ADMIT OF FILTRATION OR ANY OTHER MEANS OF SEPARATING THE DISSOLVED FROM THE UNDISSOLVED PART. 285

Treat the substance in the same manner as prescribed for a residue insoluble in water in 284.

As regards the operation to be carried out according

* The compounds of mercury, arsenic, cadmium, zinc, and, upon strong ignition, those of lead and antimony, are volatile under such conditions.

to 284, *b*, *β*, it is often advisable to boil the mass (carbonized at a gentle heat) with water, filter, examine the filtrate by itself, wash the residue, incinerate it, and examine the ash.

4. The following method, proposed by E. MILLON,* is of VERY GENERAL APPLICATION for the detection of metals when mixed with organic matter: Transfer the triturated substance to a tubulated retort, and add about four times its weight of concentrated sulphuric acid. The retort should not be more than one third full. Heat slowly till the mass is disintegrated or dissolved, and then, placing a funnel-tube in the tubulure of the retort and gently increasing the temperature, gradually add nitric acid. The object of this first operation (which will take about half an hour) is to decompose chlorides. Now remove the mixture to a platinum dish, and heat till the sulphuric acid, which by degrees loses its black color and turns orange or red, begins to escape. Add more nitric acid in small portions. After each addition, the fluid is decolorized, but it turns darker again on further heating. Continue adding nitric acid until no more coloration occurs, and finally expel the sulphuric acid, when a pure white, saline mass will be obtained, which is to be analyzed in the usual way. According to MILLON, if the heat is moderated towards the end, none of the arsenic or mercury will be lost; but this cannot be depended on when considerable quantities of chlorides are present.

5. TO SEPARATE SALTS FROM COLLOID ORGANIC MATTER, dialysis (§ 8) is often very advantageous.† The substance is brought into the dialyzer according to circumstances, sometimes directly, sometimes after warming with hydrochloric acid or even with hydrochloric acid and potassium chlorate (compare also § 261).

6. If it is not desired to use the method given in 5, which requires somewhat more time, the detection of the

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* Journ. de Pharm. et de Chim., **46**, 33; Zeitschr. f analyt. Chem., **4**, 208. In regard to a modification of MILLON'S process proposed by POUCHET, compare Zeitschr. f. analyt Chem., **21**, 306.

† Compare O. REVEIL, Zeitschr. f. analyt. Chem., **4**, 266; BIZIO, *ibid.*, **5**, 51; RIEDERER, *ibid.*, **7**, 517; H. STRUVE, *ibid.*, **24**, 72.

halogens may be effected by mixing the substance with about four parts of pure sodium carbonate, igniting the mixture for some time, and finally detecting the halogens in the colorless aqueous extract.*

7. IF THE SPECIAL OBJECT IS THE DETECTION OF ARSENIC IN FABRICS, WALL-PAPERS, AND THE LIKE, as well as in dyes (especially aniline dyes), this is attained by the following processes:

a. Pour 100 cc of pure hydrochloric acid, of 1.19 sp. gr., upon 20 to 30 g of the substance † under investigation (after cutting it into small pieces, if necessary), in a tubulated retort of about 500 cc capacity. The neck of the retort should be drawn out and bent down at an obtuse angle. Place the retort so that the part of the neck next to its body slants upward, while the other part is inclined somewhat steeply downward. The latter is introduced into the cooling-tube of a LIEBIG'S condenser, and the joint is closed with a piece of rubber tubing. The cooling-tube is connected air-tight with a tubulated receiver of about 700 cc capacity. The latter is charged with 200 cc of water, and, to keep it cool, is placed in a dish of cold water. Connect the tubulure of the receiver with a PÉLIGOT'S tube containing water. After about an hour, introduce into the retort 5 cc of a cold saturated solution of ferrous chloride prepared from the crystals, and heat the contents. After the excess of hydrogen chloride has escaped, raise the temperature so that the liquid comes to boiling, and distil until the contents begin to froth strongly. Now allow the retort to cool, again introduce 50 cc of hydrochloric acid of 1.19 sp. gr., and distil again in the same way.

Dilute with water to 600 or 700 cc, the distillate,

* Concerning other methods proposed for the same purpose, compare MARSH, Pharmac. Centralhalle, 1889, p. 515; THOMS, *ibid.*, 1893, p. 10.

† If one cannot or does not wish to use so much substance (*e g.*, in the examination of dyes), the quantities of the hydrochloric acid, ferrous chloride, etc., are to be reduced to correspond to the amount of substance. In this case, a smaller retort and receiver should be selected.

which is colored brown by organic substances and to which the contents of the PÉLIGOT's tube are added, and pass in pure hydrogen sulphide gas, first while warm, then in the cold.

After about 12 hours, filter off the brown precipitate (consisting partly or wholly of organic substances) upon an asbestus filter, which is prepared by introducing asbestus into a funnel provided with a glass stop-cock, wash the precipitate to some extent, close the stop-cock, and treat the precipitate in the funnel, while the latter is covered with a watch-glass, with a few cubic centimeters of a solution of bromine in hydrochloric acid of 1.19 sp. gr. After this has acted for about half an hour, allow the solution to run out into the precipitating-flask, upon the walls of which particles of the hydrogen sulphide precipitate are frequently still adhering. Wash the residue on the asbestus filter with the strong hydrochloric acid frequently mentioned, add ferrous chloride to the contents of the flask in sufficient excess, and rinse the whole, with the aid of the strong hydrochloric acid, into the retort of a smaller distilling apparatus similar to the one already described. Distil the liquid down rather far, let it cool, again add 50 cc of the hydrochloric acid of 1.19 sp.gr., and distil once more. Dilute the distillate, with the contents of the PÉLIGOT's tube, to about 500 or 700 cc, and treat with hydrogen sulphide as given above, to separate as arsenious sulphide any arsenic that may be present (R. FRESENIUS and E. HINTZ). If it is desired to have the arsenic as a mirror, treat the sulphide of arsenic according to 300.*

b. The method prescribed in Sweden is based upon the same principle, and is carried out, ac-

* The presence of arsenic in the substance examined cannot be considered as shown with entire certainty, however, unless a blank experiment with the same hydrochloric acid, the same ferrous chloride, and carried out in the same retort, has given a negative result. ATTERBERG (Chem. Centralbl., 1885, p. 600) prefers to evaporate the distillate containing arsenic with nitric acid, to dissolve the residue in water, and to convert the arsenic acid into silver arsenate.

cording to the most recent agreement of the Swedish commercial chemists, in the following manner:*

A flask of about 300 cc capacity is connected with an open receiver by means of a 50 cc pipette, bent twice at right angles. The receiver holds about 100 cc, and is half filled with water, into which the point of the pipette dips a little. Place the sample in the flask, add 2 g of arsenic-free ferrous sulphate, and cover with from 50 to 80 cc of arsenic-free, concentrated hydrochloric acid of 1.18 to 1.19 sp. gr. In the case of bronze colors or other metallic substances, 2 or 3 g more of arsenic-free ferrous sulphate are to be added. Heat the flask and keep the hydrochloric acid boiling as long as the pipette can be held in the hand. To the distillate obtained, either add 50 cc of saturated hydrogen sulphide water, or dilute with 50 cc of water, and pass in hydrogen sulphide gas. After standing for 12 hours, the precipitated sulphide of arsenic is filtered upon a small filter, washed until the acid reaction disappears, and then dissolved in 5 cc of dilute ammonia (1 volume of ammonia of .96 sp. gr. and 1 volume of water). After the addition of .02 g of sodium carbonate, the solution is evaporated to dryness on a watch-glass, the residue is triturated with about .3 g of a mixture of sodium carbonate and potassium cyanide, and reduced in a bulb-tube of absolutely arsenic-free glass in a stream of carbonic acid, in the well-known manner. The bulb-tube is fashioned in such a way that the narrow part in which the arsenic should deposit is attached directly to a bulb of about 2 cm diameter.

c. If a dye is under investigation, mix it with 2 parts of sodium carbonate and 2 parts of sodium nitrate, or soak the fabric or wall-paper with a concentrated solution of this mixture, and dry completely. Then fuse some sodium nitrate in a small dish of genuine porcelain, and, with continued heating, gradually introduce the substance prepared according to

* Compare Zeitschr. f. analyt. Chem., 34, 89.

the foregoing directions, while more sodium nitrate is added from time to time, if necessary. A mass is thus obtained which is free from carbon and organic substances. After cooling, soak it out with water, filter off the alkaline liquid, wash the residue, add to the filtrate and washings as much dilute sulphuric acid as is necessary to expel the carbonic, nitrous, and nitric acids, then evaporate, at first upon the water-bath, finally at a somewhat elevated temperature, until heavy sulphuric acid vapors begin to escape, allow the residue to cool, dilute and filter. This liquid may now be used directly in the MARSH apparatus, in order to test it for an arsenic mirror (§ 155, 10), or it may be precipitated with hydrogen sulphide after the addition of a few drops of hydrochloric acid, and any precipitate resulting may be treated according to **300**.

d. As is easily perceived, in many cases a simpler process will suffice for obtaining from wall-papers, fabrics, etc., a liquid which may be tested directly in the MARSH apparatus. Of the many methods proposed for this purpose, only the one recommended by H. FLECK will be given.*

Digest the object of investigation, finely cut up, for from 18 to 24 hours at 50° or 60°, with 50 or 100 g of pure 25 per cent sulphuric acid. If any coloring matter is still visible upon the object after the digestion (which is very seldom the case) add from 3 to 5 g of pure nitric acid of 1.24 sp. gr. for 100 g of the 25 per cent sulphuric acid, and continue the digestion until all the remnants of color are destroyed. Filter, wash, dilute to 200 cc, and test the liquid in MARSH'S apparatus, adding it in portions of 20 cc. If nitric acid has been added, the liquid must be evaporated until all of this is removed, before diluting to 200 cc.†

* Zeitschr. f. analyt. Chem., **22**, 474.

† As regards other methods proposed for the same purpose, compare H HAGER, Zeitschr. f. analyt. Chem., **11**, 478; E. LYTTKENS, *ibid.*, **22**, 147; G THOMS, *ibid.*, **22**, 475; POLENSKE, Pharmac. Centralhalle, 1889, p. 868.

e. In the solution prepared according to *d*, the arsenic may, of course, be detected by one of the rapid methods given in § 157, 7, *e* or *f*, instead of using MARSH'S apparatus.

8. In relation to the official prescription for establishing the presence of arsenic and tin in colored articles of food, compare Zeitschr. f. analyt. Chem., **27**, 471.

9. For the detection of iodine in urine, the following methods are recommended:

a. If the urine is clear and but little colored, the iodine is usually easily detected by mixing the urine in a test-tube with a little carbon disulphide, a drop of a solution of nitrous acid in concentrated sulphuric acid, and shaking (§ 184, 10). If the urine should have an alkaline reaction, acidify it first with dilute sulphuric acid.

b. If the character of the urine does not admit of making the test in the simple manner described in *a*, evaporate it to dryness with the addition of some caustic potash, ignite the residue gently for a long time, treat it with water, filter, acidify with dilute sulphuric acid, and detect the iodine in the solution according to § 184, 8 or 10.*

2. *Detection of Inorganic Poisons in Articles of Food, in Dead Bodies, etc., in Chemico-legal Cases.* †

§ 258.

The chemist is sometimes called upon to examine an article of food, the contents of a stomach, a dead body, etc., with a view to detect the presence of some poison, and thus to establish the fact of accidental or wilful poisoning. It is more frequently the case, however, that the question put to him is of a less general nature, and **286**

* Concerning other methods for detecting iodine in urine, compare F. PECIRKA, Chem. Centralbl., 1883, p. 626; E. HARNACK, *ibid.*, 1884, p. 83; C. SCHWARZ, *ibid.*, 1887, p. 1525; A. F. JOLLES, Zeitschr. f. analyt. Chem., **30**, 288, and **33**, 543.

† Compare FRESENIUS, Ann. d. Chem. u. Pharm., **49**, 275; and FRESENIUS and v. BABO, Ann. d. Chem. u. Pharm., **49**, 287.

that he is called upon to determine whether a certain substance placed before him contains a metallic poison, or, more pointedly still, whether it contains arsenic or hydrocyanic acid, or some other particular poison; for it may happen either that the symptoms point clearly to a certain poison, or that the examining magistrate has, or believes he has, some other reason to put such a question.

It is obvious that the task of the chemist will be the easier, the more special and pointed the question which is put to him. However, the analyst will always act most wisely, even in cases where he is simply requested to state whether a certain poison (*e.g.*, arsenic) is present, if he adopts a course which will not only permit the detection of the one poison specially named, the presence of which may perhaps be suspected on insufficient grounds, but will also inform himself as to the presence or absence of other similar poisons.

But we must not go too far in this direction, for if an attempt were made to devise a method that would embrace all poisons, we might succeed in elaborating such a method at the writing-desk, but experience would speedily show that the complexity inseparable from such a course must impede the execution of the process, and impair the certainty of the results to such an extent that the drawbacks would be greater than the advantages to be derived from it.

Moreover, the attending circumstances usually permit at least a tolerably safe inference as to the group to which the poison belongs. Acting on these views, the following methods are here given:

1. A method which insures the detection of the minutest traces of arsenic that can be taken into consideration in legal investigations, allows of its quantitative determination, and at the same time permits the detection of all other metallic poisons.

2. A method to effect the detection of hydrocyanic acid, which leaves the substance still fit to be examined both for metallic poisons and for alkaloids.

3. A method to effect the detection of phosphorus,

which does not interfere with the examination for other poisons.

This part of the book, therefore, is not designed to be a complete guide in every possible case of chemico-legal investigation. The instructions given, however, are the tried and proved results of personal experience. Moreover, they will generally be found sufficient, especially as in the section on the alkaloids, a description is given of the best processes by which the detection of these poisons may be effected in legal cases.

Where there are no indications of the sort of poison to be looked for, so that it is necessary to take all poisons, both inorganic and organic, into consideration, begin by carefully inspecting the substance, with the aid of a microscope if necessary, by noting the odor, reaction, etc., and then, if the circumstances permit, proceed to examine separate portions for the different classes of poisons. Test for hydrocyanic acid and phosphorus (a single distillation usually suffices for the detection of both), afterwards for alkaloids, and finally for metallic poisons. If various objects are to be examined, such as food, vomit, contents of the stomach, of the intestines, urine, organs (liver, spleen, etc.), it is important, as a rule, that each object should be examined separately. As an obvious matter of caution, one third of the substance, after weighing and mixing, should always be reserved for unforeseen contingencies, and, if the case requires it, for determining in what state of combination a suspicious element which is found exists.

I. Method for the Detection of Arsenic (with due Regard to the possible Presence of other Metallic Poisons.)

§ 259.

Of all metallic poisons, arsenic is the most dangerous 287
and the most frequently used for the wilful poisoning of others. Among the compounds of arsenic, arsenious oxide (white arsenic) occupies the first place, because it kills even in small doses, it does not betray itself (or at

least very slightly) by the taste, and it is readily procurable.

As arsenious oxide dissolves in water only sparingly, and (on account of the difficulty with which moisture adheres to it) very slowly, the greater portion of the quantity swallowed usually exists in the body in the undissolved state. Moreover, as the smallest grains of it may be readily detected by means of an exceedingly simple experiment; and (even though arsenic occurs in other compounds in ochres, colored cloths, etc.) as it is certain that arsenious oxide in grains or powder is never normally present in foods, in the human body, or in the contents of decayed coffins,* the particular care and efforts of the analyst ought always to be directed to the detection of the arsenious oxide in substance, and this end may be usually attained. In searching for the oxide, metallic arsenic (which may be also used for poisoning) may be found in the same way in case it is still present as such.

A. Method for the Detection of undissolved Arsenious Oxide or Metallic Arsenic.

§ 260.

1. If food, vomit, or some other matter of the kind is to be examined, weigh it, mix the whole as uniformly as may be practicable, reserving one third for contingencies, and mix the other two thirds in a porcelain dish with distilled water. Let the mixture stand a little, then pour off the fluid, together with the lighter suspended particles, into another porcelain dish. Repeat the latter operation several times, if possible with the same fluid, pouring it from the second dish back into the first and so on. Finally, wash once more with pure 288

* I was once intrusted with the examination of the entirely decomposed remains of a long buried child, which were in a small coffin painted with ochre. The cover of the coffin had a decayed opening, so that the decomposed wood was mixed with the remains. The contents of the coffin contained a very small amount of arsenic, but not more than the ochre paint on a surface of the coffin-cover equal to that which had fallen in. The remains of the body as such, therefore, contained no arsenic.

water (best in a glass dish), remove the fluid as far as practicable, and observe whether any small, white, hard grains which feel gritty under the glass rod (arsenious oxide), or also any black grains or scales (metallic arsenic), are to be found in the dish. If not, proceed as directed in § 261 or § 262. But if so, pick out the suspected grains, or some of them, if possible, with a pair of pincers, or, if they are very minute, wash them further in a watch-glass, dry and weigh them, and heat a small portion in a glass tube. Arsenious oxide gives a sublimate consisting of small, brilliant octahedrons or tetrahedrons, while metallic arsenic gives a mirror at once. If the former sublimate is obtained, test another fragment as to its behavior upon heating with a splinter of charcoal (§ 155, 2). If the last experiment gives an arsenic mirror, it is quite safe to conclude that the grains consist of arsenious oxide. If it is desired to determine the quantity of the arsenic, or to test for other metallic poisons, unite the contents of both dishes, and proceed as directed in § 261 or § 262.

2. If a stomach is submitted for analysis, empty the contents into a porcelain dish, turn the stomach inside out, and (*a*) search the inside coat for small, white, hard, sandy grains, or, as the case may be, for black grains or scales. The spots occupied by such grains are often reddened, and the grains are also frequently found firmly imbedded in the membrane. (*b*) Mix the contents in the dish uniformly, weigh them, put aside one third for contingencies, and treat the other two thirds as in 1. The same course is also pursued with the intestines. In other parts of the body (with the exception perhaps of the pharynx and œsophagus), arsenious oxide or metallic arsenic cannot be found in grains, if the poison has been introduced through the mouth. If grains of the kind described have been found, examine them as directed in 1; if not, or if it is desired to test also for other metallic poisons, proceed according to § 261 or § 262.

*B. Method of detecting soluble Arsenical and other Metallic Compounds by means of Dialysis.**

§ 261.

If method *A* has failed to show the presence of 289
arsenious oxide in the solid state, and the process (described in § 262) in which organic matter is coagulated or destroyed by potassium chlorate and hydrochloric acid is at once resorted to, the operator must, in the event of the presence of arsenic being revealed, give up all notion of ascertaining, as far as the portion operated upon is concerned, in what form the poison has been administered; for the process will give a solution containing arsenic acid, no matter whether the poison was originally present in that form, or as arsenious oxide, or as sulphide, or in the metallic state, etc. This defect may be remedied, however, by interposing a dialytic experiment between the operations described in *A* and *C*.

The experiment requires the apparatus shown in Fig. 6, § 8. The hoop is made of wood, or, better, of gutta-percha; it is 6 cm in depth, and 20 to 30 cm in diameter. When the dialyser has been set up in perfect condition, the residue and fluid of § 260 (having been mixed, if the case requires it, with two thirds of the stomach, intestinal canal, etc., cut small, and the whole, digested for 24 hours at about 32°) are poured into the dialyser to the depth of not more than 15 mm. The dialyser is then floated in a vessel containing about four times as much water as the fluid to be dialysed amounts to. After 24 hours, one half or three fourths of the crystalloids will be found in the external water, which generally appears colorless. Concentrate this by evaporation on the water-bath, acidify the greater part with hydrochloric acid, treat with hydrogen sulphide, and proceed as directed in 291. If an arsenical compound soluble in water (or some other soluble metallic salt) is present, the corresponding sulphide is obtained almost pure. By floating the dialyser successively on fresh supplies of water, the

* Compare § 8.

whole of the soluble crystalloids present may be finally withdrawn. If arsenic is found, test the remainder of the concentrated dialysate according to § 157, 12, to see whether arsenious or arsenic acid is present.

It is generally best to examine the exhausted contents of the dialyser at once, according to § 262, for compounds of metals insoluble in water, but in some cases (for instance, when it is wished to determine the state of oxidation or combination of compounds of arsenic or other metals), it is preferable to heat the matter first with dilute hydrochloric acid, and to dialyse it again.

Instead of interposing the dialysis at this stage (and thus lengthening the time of the investigation), it may be better to wait till the close of the operation described in *C*, and then if a metallic poison has been found, and it is desired to ascertain its state of oxidation and form of combination (compare **308**), recur to this paragraph, using the reserved one third for the experiment. This method is to be preferred in most cases.

*C. Method for the Detection of Arsenic in whatever Form it may exist, which allows also of its Quantitative Determination, and of the Detection of all other Metallic Poisons.**

§ 262.

If no arsenious oxide or metallic arsenic has been found as such, by the method described in *A*, nor a soluble arsenical compound by dialysis, evaporate the mass (which has been diluted by washing) to a pasty consistence (if it should be acid, after the addition of pure sodium carbonate until this is just in excess) in a porce-

*The following process is essentially that which I worked out and published in association with L. v. BABO in 1844 (compare Ann. d. Chem. u. Pharm., **49**, 308). I have since used it in many cases, and have had it used under my supervision, and it *has always been trustworthy*. Concerning the distribution of arsenic in the animal organism after the incorporation of arsenious acid, compare E. LUDWIG, Zeitschr. f. analyt. Chem., **20**, 608. [GAUTIER'S process for the detection of arsenic, as modified by JOHNSON and CHITTENDEN, is speedy and simple, and requires but few reagents, all of which may be purchased absolutely free from arsenic. (See Amer. Chem. Jour., **2**, 235, and **5**, 8.)]

lain dish, on the water-bath, adding, if occasion requires, two thirds of the stomach and intestines, cut small, provided this has not been done already in the process of dialysis. In examining other parts of the body (the lungs, liver, etc.), cut them also into small pieces, and use two thirds for the analysis. If, from any cause, the substance to be treated should contain alcohol, this should first be removed under all circumstances, by evaporation.

The process is divided into the following parts:*

* It is self-evident that only such utensils and reagents can be used for such an investigation as those concerning which the operator is convinced by the most careful selection and testing, that they are free from arsenic, heavy metals in general, and other impurities. The process to be described requires the following reagents: 1. *Hydrochloric acid*, 1.10 to 1.12 sp. gr.—(In addition to the method given in § 29 for the preparation of arsenic-free hydrochloric acid, that recommended by BECKURTS, Zeitschr. f. analyt. Chem., 24, 483, answers the purpose well.) Although the examination of hydrochloric acid in regard to its purity has already been mentioned in § 29, still attention must be called to the fact that extraordinary care is necessary in testing it for arsenic, because the acid is used in considerable amount. For delicate testing for this metal, the following methods are especially appropriate: *a*. Heat 1 liter of the acid with the addition of some *pure* ferrous chloride or ferrous sulphate in a distilling apparatus, and test the first 50 cc which go over, by means of arsenic-free zinc, to find whether it shows itself free from arsenic in testing according to the methods given in § 157, 7, *e* and *f*; also whether it gives no trace of an arsenic coating in the glass tube in the apparatus described in § 155, 10, even after continuing the experiment for a long time. *b*. Evaporate 1 liter of the acid down to a small residue in a dish of genuine porcelain, after the addition of some water and a *few* fragments of pure potassium chlorate, adding some water from time to time, and test the residue as directed in *a*, in MARSH'S apparatus (ROB. OTTO, in FR. J. OTTO'S "Anleit zur Ausmittelung der Gifte," sechste Aufl., von ROB. OTTO, p. 146). The *ferrous chloride* required for testing in *a* is prepared by dissolving iron wire in pure hydrochloric acid of 1.10 to 1.12 sp. gr., and heating the solution for a long time in a distilling apparatus. As soon as no traces of arsenic are to be detected in the distillate, the ferrous chloride is free from arsenic. If ferrous sulphate is used, this must be tested in the same way by heating with concentrated hydrochloric acid in a distilling apparatus. 2. *Potassium chlorate*.—The safest way to test this is to heat a large quantity with twice its weight of water to boiling, and to allow it to crystallize while being stirred. Then place the mass of salt upon a funnel, allow the mother-liquor to drain off, decompose the latter by warming it with dilute arsenic-free hydrochloric acid, and test a portion with hydrogen sulphide and afterwards with ammonium sulphide for any heavy metals. Evaporate another portion to a small volume, with occasional addition of some water, and test the solution of this in MARSH'S apparatus. 3. *Hydrogen sulphide gas*.—Since the hydrogen sulphide produced by the action of hydrochloric or sulphuric acid upon iron sulphide

1. *Decoloration and Solution.*

Add to the matter in the porcelain dish (which, for ex- 290
ample, may amount to 100 or 250 g) a quantity of pure

often contains some hydrogen arsenide, in consequence of the presence of arsenic in the materials, the gas should not be prepared in this way for legal investigations, or, at least, not without previous purification. In such cases, the gas must either be evolved from arsenic-free materials, or, if produced in the usual way, it must be purified before use. Several methods of purification which serve the purpose have been recently recommended, viz., combining the hydrogen sulphide with magnesia to form hydrosulphide (DIVERS and SHIMIDZU, Zeitschr. f. analyt. Chem., **24**, 243); passing the gas over potassium sulphide heated to 350° (O. v. D. PFORDTEN, Ber. d. deutsch. chem. Gesellsch., **17**, 2897); washing the gas by a system of bottles containing hydrochloric acid of varying concentration (W. LENZ, Zeitschr. f. analyt. Chem., **22**, 393); or passing the gas over dry iodine (JACOBSEN, *ibid.*, **29**, 737; O. BRUNN, Chem. Centralbl., 1888, p. 1376). Nevertheless, I consider it much safer to evolve the gas from arsenic-free materials, and, in fact, from *calcium sulphide* or *barium sulphide* which has been produced by igniting gypsum or heavy-spar with carbon. According to KOSMANN, barium sulphide has been in use for the purpose of evolving hydrogen sulphide, for at least 30 years in the laboratory of the École des Mines in Paris, directed by RIVOT. Calcium sulphide has been recommended by ROB. OTTO (FR. J. OTTO'S "Anleit. zur Ausmittelung der Gifte," 6te Aufl., von Dr. ROB. OTTO, p. 158). He recommends the following method for preparing it and for evolving the gas: Make a stiff paste from 7 parts of dehydrated gypsum, 3 parts of charcoal powder, and 1 part of rye flour, with water; form this into balls or cylinders; dry it completely, and ignite it in a well-covered Hessian crucible at a strong, bright red heat. Place the coarsely broken calcium sulphide in a WOULFE'S bottle, one tubulure of which is provided with a funnel having a glass stop-cock, while the delivery-tube is inserted in the other. If pure hydrochloric acid is allowed to flow from the funnel-tube, drop by drop, upon the calcium sulphide, which is covered with water, a pretty constant stream of pure hydrogen sulphide is evolved, if the apparatus is shaken sufficiently. Concerning other methods of producing arsenic-free hydrogen sulphide, compare Zeitschr. f. analyt. Chem., **23**, 280; O. v. D. PFORDTEN, Ber. d. deutsch. chem. Gesellsch., **17**, 2898; HAMPE, Zeitschr. f. analyt. Chem., **31**, 557. 4. *Red, fuming nitric acid.*—For the purpose of testing this, evaporate a large portion upon the water-bath to dryness, and test the aqueous solution of any residue left, on the one hand with hydrogen sulphide and ammonium sulphide, and on the other, in MARSH'S apparatus. 5. *Concentrated sulphuric acid.*—The testing of this has already been mentioned in § 25. The experiment with the MARSH'S apparatus must be continued for a long time in order to obtain a reliable result. 6. *Sodium carbonate.*—For testing this, see § 49. 7. *Sodium nitrate.*—This must give a clear solution with water. The solution ought not to give a yellow precipitate when heated with the solution of ammonium molybdate in nitric acid (§ 156, 9). Hydrogen sulphide ought not to give a precipitate in the acidified solution, nor ammonium sulphide in the neutral one. 8. *Potassium cyanide.*—For testing this, see § 57. It should never be neglected to prove

hydrochloric acid, of 1.10 to 1.12 sp. gr., about equal to or somewhat exceeding the weight of the dry substances present, and sufficient water to give to the entire mass the consistence of a thin paste. The quantity of hydrochloric acid added should never exceed one third of the entire liquid present. In the very first place add to this about 2 g of potassium chlorate,* and heat upon the water-bath. When the liquid has attained the temperature of the water-bath, add more potassium chlorate in portions of from .5 to 2 g, at intervals of 5 or 10 minutes, with stirring, until the contents of the dish are nearly homogeneous and fluid, and also as a rule have become light yellow, and this color is retained upon continuing the heating for 15 or 30 minutes longer. Replace the evaporating water from time to time. When this point is attained, add again a portion of potassium chlorate, and then remove the dish from the water-bath. When the contents are quite cold, transfer them cautiously to a linen strainer or a filter (according to the quantity), allow the whole of the fluid to pass through, and heat the filtrate on the water-bath with renewal of the evaporating water, until the smell of chlorate has nearly or quite disappeared. Wash the residue well with hot water, dry it, designating it as I, and reserve it for further examination, according to **302**. Evaporate the washings on the water-bath to about 100 cc, and add this liquid, together with any precipitate that may have formed therein, to the principal filtrate.†

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that this reagent, when mixed with pure sodium carbonate in a porcelain boat and heated persistently in the apparatus described in § 155, 13, gives no trace of a dark deposit in the glass tube. 9. Test the washed *filter-papers* used, by moistening a number of them with hydrochloric acid, then allowing them to stand for a long time, washing out the hydrochloric acid with some water, and testing the dilute acid thus obtained, according to 1.

* If it is not wished to introduce potassium into the mass, instead of potassium chlorate, pure chloric acid (as recommended by SONNENSCHEIN and JESSERICH, Zeitschr. f. analyt. Chem., **22**, 472) may be employed with the best success.

† The frequently expressed fear that arsenic, antimony, or tin might volatilize during the treatment described I have shown to be unfounded from repeated experiments in which hydrochloric acid of the same concentration was used (1 part of hydrochloric acid of 1.12 sp. gr., to 2 parts of water).

In the case of urine, the treatment with hydrochloric acid and potassium

2. *Treatment of the Solution with Hydrogen Sulphide.* 291
(Separation of the Arsenic as Sulphide, or of all the metals of Groups V and VI in the form of Sulphides.)

Transfer the fluid obtained in 1 (which amounts to about four times the quantity of the hydrochloric acid used) to a flask, heat it on the water-bath to 70°, and transmit through it, for about 12 hours, a slow stream of washed hydrogen sulphide, then let the mixture cool, continuing the transmission of the gas; rinse the delivery-tube with some ammonia, acidify the ammoniacal solution thus obtained, and add it to the principal fluid, cover the flask lightly with filter-paper, and put it in a moderately warm place (about 30°) until the odor of hydrogen sulphide has nearly disappeared. Collect the resulting precipitate on a rather small filter, and wash with water containing hydrogen sulphide *until the washings are free from chlorine.* Concentrate the filtrate and washings after saturating them again with hydrogen sulphide. If a precipitate forms, filter it off, wash, and add to it the principal hydrogen sulphide precipitate. In a flask of proper size mix the concentrated fluid with ammonia to alkaline reaction, then with ammonium sulphide ; closely cork the flask, which must now be nearly full, and reserve it for further examination according to **306.**

3. *Purification of the Precipitate produced by Hydrogen Sulphide.* 292

The precipitate obtained in 2 contains the whole of the arsenic and all the other metals of the fifth* and sixth

chlorate is usually unnecessary. After being acidified with hydrochloric acid it may usually be subjected to the treatment with hydrogen sulphide prescribed in **291.**

Many other methods of destroying organic matter have been proposed, a summary of which is to be found in G. DRAGENDORFF'S work, "Die gerichtlich-chemische Ermittelung von Giften," 3. Aufl., p. 352 *et seq.* In addition, attention may be called to the method recommended by ZUCCO (Chem. Centralbl., 1888, p. 1598).

* Lead sulphide and cadmium sulphide do not precipitate from very acid solutions. If lead or cadmium should remain in solution on this account, it is found in the precipitate by ammonium sulphide (**306**). When mercury was present, only a part of it may have gone into solution under certain circumstances (LECCO, LUDWIG); the rest of it is found in Residue I (compare **302**).

groups, in the form of sulphides, and also organic matter and free sulphur. Dry it completely with the filter in a small porcelain dish, over the water-bath, add pure, fuming nitric acid (entirely free from chlorine), drop by drop, until the mass is completely moistened, then evaporate to dryness on the water-bath, and repeat this treatment with nitric acid if necessary. Moisten the residue uniformly with pure concentrated sulphuric acid, previously warmed, then heat for 2 or 3 hours on the water-bath, and finally with an air-, sand-, or oil-bath at a somewhat higher, though still moderate, temperature (170°), until the charred mass becomes friable, and a small sample of it (to be returned afterwards to the mass) when mixed with water and then allowed to subside, gives a colorless or almost colorless, but not brownish, fluid; should the aqueous fluid be brownish, or should the residue consist of a brown oily liquid, add to the mass some pieces of pure, well-washed, fine, dry filter-paper, and continue the application of heat. The heat may be raised till fumes of sulphuric acid begin to escape, without fear of loss of arsenic. By attending to these rules, the object in view will always be completely attained, viz., the destruction of the organic substances, without loss of any of the metals. Warm the residue a little on the water-bath with a mixture of 8 parts of water and 1 part of hydrochloric acid; filter, wash the undissolved part repeatedly with small amounts of hot water containing a little hydrochloric acid, complete the washing with boiling water, and to the filtrate add the washings, concentrated, if necessary, by the evaporation of the last wash-water upon the water-bath.

Dry the washed carbonaceous residue, then mark it II, and reserve it for further examination according to 303.

4. *Preliminary Examination for Arsenic and other Metallic Poisons of Groups V and VI.* (Second Precipitation with Hydrogen Sulphide.) 293

The clear, colorless, or, at the most, somewhat yellowish fluid obtained in 3 contains all the arsenic in the

form of arsenious acid, and may also contain tin, antimony, mercury, copper, bismuth, and cadmium. Gradually supersaturate a small portion with a mixture of ammonium carbonate and ammonia, and observe whether a precipitate is produced. When this question has been decided, acidify the portion with hydrochloric acid, which will redissolve the precipitate that may have been produced by ammonium carbonate, then return the sample to the principal fluid, and treat the latter persistently with hydrogen sulphide, first at a gentle heat, afterwards without heat, exactly according to **291**.

This process may lead to three different cases, which are to be carefully distinguished, as follows:

294 *a. Hydrogen sulphide fails to produce a precipitate, even after a long time;* but on standing, a trifling white or yellowish-white precipitate separates. In all probability, in this case, no metals of Groups V and VI are present. Nevertheless, treat the filtered and washed precipitate as directed in **297**, to guard against overlooking even the minutest traces of arsenic, etc.

295 *b. A precipitate is formed of a pure yellow color,* like that of arsenious sulphide. Take a small portion of the fluid, together with the precipitate suspended therein, add some ammonium carbonate, and shake for some time without heating. If the precipitate dissolves readily and (with the exception of a trace of sulphur) completely, and if in the preliminary examination (**293**) ammonium carbonate has failed to produce a precipitate, arsenic alone is present (at least, if any tin or antimony is present its amount is very slight). Mix the solution of the small sample in ammonium carbonate, with hydrochloric acid to acid reaction, return this to the fluid containing the principal precipitate, and proceed as directed in **297**. If, on the other hand, the addition of ammonium carbonate to the sample completely or partially fails to redissolve the precipitate, or if, in the preliminary examination (**293**), ammonium carbonate has produced a precipitate, there is reason

to suppose that another metal is present, perhaps with arsenic. In this latter case, also, add to the sample in the test-tube, hydrochloric acid to acid reaction, return it to the fluid containing the principal precipitate, and proceed as directed in **298**.

c. A precipitate is formed of another color. In that case, it must be assumed that other metals are present, perhaps with arsenic. Proceed as directed in **298**. **296**

5. *Treatment of the Yellow Precipitate produced by Hydrogen Sulphide, when the Results of* **295** *lead to the Assumption that Arsenic alone is present.* (Determination of the Weight of the Arsenic.) **297**

As soon as the fluid precipitated according to **293** has nearly lost the smell of hydrogen sulphide, collect the yellow precipitate, if its amount is considerable, on a small filter, which has been dried at 100° and weighed; wash it first with water, then with absolute alcohol, and finally with pure benzol or petroleum-ether, in order to remove any admixed sulphur. After the benzol or petroleum-ether has been removed with absolute alcohol, dry the precipitate and filter at 100° to constant weight. If, on the other hand, the precipitate is very slight, free it from intermixed sulphur in the same way as described above, wash it at last with water, and dissolve it in ammonia-water; then wash the filter (upon which nothing should remain undissolved in this case) completely with dilute ammonia, evaporate the ammoniacal liquid in a small, accurately weighed porcelain crucible on the water-bath, and dry the residue at 100° until the weight no longer diminishes, and weigh it. The final weight of the precipitate upon the filter, or the residue in the dish, represents the quantity of arsenious sulphide, if upon the subsequent reduction this is found to be pure. In that case multiply the weight by .8049 to obtain the corresponding amount of arsenious oxide, or by .6098 to obtain the corresponding amount of metallic arsenic. Proceed with the precipitate, or the residue in the dish, according to **300**.

6. *Treatment of the Yellow Precipitate produced by Hydrogen Sulphide when the Results of* **295** *or* **296** *lead to the Assumption that another Metal is present, perhaps with Arsenic.* (Separation of the Metals from each other. Determination of the weight of the Arsenic). **298**

If there is reason to suppose that the fluid precipitated according to **293** contains other metals, perhaps with arsenic, proceed as follows: As soon as the precipitation is fully completed, and the smell of hydrogen sulphide has nearly disappeared, collect the precipitate on a small filter, wash thoroughly, pierce the point of the filter, and wash all the precipitate into a small flask, using the least possible quantity of water. Add to the fluid in which the precipitate is now suspended, first ammonia, then some yellowish ammonium sulphide, and let the mixture digest for some time at a gentle heat. Should part of the precipitate remain undissolved, filter this off, wash, pierce the filter, rinse off the residuary *precipitate*, mark it III, and reserve for further examination, according to **304**. Evaporate the *solution* or the *filtrate*, together with the washings, to dryness in a small porcelain dish. Treat the residue with some pure fuming nitric acid (free from chlorine), nearly drive off the acid by evaporation, then add (as C. MEYER was the first to recommend) a solution of pure sodium carbonate, in small portions, till in excess. Add now a mixture of 1 part of sodium carbonate and 2 parts of the nitrate, in sufficient yet not excessive quantity, evaporate to dryness, and heat the residue very gradually to fusion. Let the fused mass cool, and take it up with cold water. If a residue remains undissolved, **299** filter, wash with a mixture of equal parts of alcohol and water, mark it IV, and reserve for further examination, according to **305**. Mix the solution, which must contain all the arsenic as sodium arsenate,* with the washings (previously freed from alcohol by evaporation), cau-

* If the substance under investigation should contain a thallium compound, then all the arsenic would not be in the solution, because upon treating the orange-colored compound of sulphides of thallium and arsenic (see § 130) with ammonium sulphide, the sulphide of arsenic is only incompletely dissolved. (Compare **304**.)

tiously add pure dilute sulphuric acid to strongly acid reaction, evaporate in a small porcelain dish, and when the fluid is strongly concentrated, again add sulphuric acid, to see whether the quantity first added has been sufficient to expel all the nitric and nitrous acids, then heat cautiously until heavy fumes of sulphuric acid begin to escape. To the residue, after cooling, add 5 or 10 cc of an aqueous solution of sulphurous acid in order to reduce arsenic acid to arsenious acid, heat on the water-bath until the excess of sulphurous acid has escaped, dilute somewhat with water, transfer the solution to a small flask, keep heated at 70°, and conduct into it for at least 6 hours a slow stream of washed hydrogen sulphide gas. Let the mixture finally cool, continuing the transmission of the gas all the while. If arsenic is present, a yellow precipitate will form. When the precipitate has completely subsided, and the fluid has nearly lost the smell of hydrogen sulphide, filter, wash the precipitate in the manner described in **297**, and determine its weight according to one of the methods given in the same place.

7. *Reduction of the Arsenious Sulphide.*

300 The production of metallic arsenic from the sulphide, which may be regarded as the keystone of the proof of the presence of arsenic, demands the greatest care and attention. The method recommended in § 155, 13, viz., to fuse the arsenical compound, mixed with potassium cyanide and sodium carbonate, in a porcelain boat in a slow stream of carbon dioxide, is the best and safest, affording, besides the advantage of great accuracy, also a positive guarantee against the chance of confounding the arsenic with any other body, more particularly antimony. On this account, it is especially adapted for medico-legal investigations. Take care to have the whole apparatus filled with carbon dioxide, that the contents of the boat are completely dry and do not spatter upon heating, and to regulate the stream of gas properly before heating. The heating directly in a glass tube, of the mixture of potassium cyanide, sodium carbonate, and the substance to be tested for arsenic, can be permitted only when a fusion

in another piece of the same tube with potassium cyanide and sodium carbonate in a slow stream of carbonic acid has given no trace of an arsenic coating. (Compare § 155, 13). Carbonic acid generators which do not admit of regulating the current of gas ought not to be used for the important experiment under consideration.

The sulphide of arsenic obtained may be used directly for reduction. In case it has been possible to collect it upon a weighed filter, take only a small part, so that the reduction can be repeated, if necessary. If, on the other hand, the precipitate of sulphide of arsenic was so slight that it was necessary to remove it from the filter with ammonia, again dissolve the residue (obtained by evaporating the ammoniacal solution) in a little ammonia, add .02 to .04 g of pulverized, anhydrous sodium carbonate,* evaporate to dryness on the water-bath, with stirring, and take a portion of the mass for the reduction.†

When the operation is finished, cut off the reduction- 301
tube (Fig. 46) between the narrow part and the place

Fig. 46.

where the boat was, preserve the part containing the arsenical mirror, cover the boat with water, filter after the mass of salts has become softened, acidify the filtrate with hydrochloric acid, pass in hydrogen sulphide, and notice whether a precipitate is thus produced. If pure sulphide of arsenic has been reduced, a very slight, yellow precipitate of sulphide of arsenic may be formed.‡ If traces of antimony were present in the aqueous solution

* Blemquist prefers sodium bicarbonate, because in using this, the residue is more easily removed from the crucible.

† Even with an amount of arsenious sulphide corresponding to $\frac{1}{100}$ mg of arsenious oxide, a distinctly recognizable mirror is obtained (W. Fresenius, Zeitschr. f. analyt. Chem., 20, 531).

‡ In the reduction of an amount of arsenious sulphide corresponding to 1 mg of arsenious oxide, W. Fresenius obtained no recognizable precipitate (Zeitschr. f. analyt. Chem., 20, 533).

of the fused mass, the precipitate would have an orange color, and would be insoluble in ammonium carbonate. After all the soluble salts of the fused mass have been dissolved, examine any metallic residue which may be left, for traces of tin and antimony (nothing but traces of these two metals could be present here if the instructions given have been strictly followed). Should appreciable traces of these metals, or either of them, be found, proper allowance must be made for this in calculating the weight of the arsenic.

8. *Examination of the reserved Residues, for other Metals of Groups V and VI.*

a. RESIDUE I. (Compare 290.) 302

This may contain silver chloride, metallic mercury,* albuminate of mercury,* and lead sulphate†; possibly also lead chloride, basic bismuth chloride, stannic oxide, and barium sulphate.

α. In the first place, in order to determine whether the residue contains mercury, after thorough mixing, dry a part of it, treat it with red, fuming nitric acid, warming it with this for a considerable time; evaporate to a small volume, then heat the residue with water to which some nitric acid is added, allow the liquid to cool, filter, dilute, and pass in hydrogen sulphide. If a black precipitate is obtained, filter it off, and test it according to 133, to find whether it is mercuric sulphide or whether it contains this, possibly together with bismuth sulphide or lead sulphide. If mercury is present, the whole residue must be treated like the portion, if the metals are to be determined quantitatively. In this case, bismuth and lead (if they have been found) are to be determined in the solu-

* Metallic mercury dissolves only with difficulty by treatment with hydrochloric acid and potassium chlorate (LECCO). Mercuric chloride may be held back by albuminates (LUDWIG).

† In relation to the special detection (*a*) of SILVER in animal substances, compare NICKLES, Zeitschr. f analyt. Chem., 2, 114; V. LEHMANN, *ibid.*, 21, 470; (*b*) of LEAD, A. GUSSEROW, *ibid.*, 1, 120; V. LEHMANN, *ibid.*, 21, 470.

tion obtained by heating the mercuric sulphide with nitric acid.

β. Incinerate the residue freed from mercury, or not containing it, in a porcelain dish, consume the carbon with the aid of some ammonium nitrate, extract the residue completely with water, dry the insoluble part, and fuse it for a long time in a porcelain crucible with sodium carbonate and potassium cyanide. After cooling, exhaust the mass with water, treat the residue first with dilute acetic acid in order to dissolve any barium carbonate that may have formed, warm the residue, usually remaining, with nitric acid, and examine the nitric acid solution according to **109**, then examine any residue left insoluble by nitric acid, according to § 239. Acidify the aqueous extract of the potassium cyanide fusion with nitric acid, and, if this causes a turbidity, let it settle, filter, and test it (since traces of silver may have gone into the potassium cyanide solution) for silver, according to § 135, 10. In order not to overlook traces of lead possibly present here, test a portion of the acetic acid solution, obtained above, with hydrogen sulphide, and then test the remainder of it, or, if the case requires it, the solution filtered from any lead sulphide, with gypsum solution for barium.

b. RESIDUE II. (Compare **292**.) **303**

The carbonaceous residue obtained by purifying the crude hydrogen sulphide precipitate with nitric and sulphuric acids, which may contain especially lead,* mercury,† and tin, and also bismuth, antimony,

* See the last foot-note.

† In relation to special methods of detecting *mercury* in animal substances, compare L. RIEDERER, Zeitschr. f. analyt. Chem., **7**, 517; MAYENÇON and BERGERET, *ibid.*, **13**, 103; E. LUDWIG, *ibid.*, **17**, 395, **20**, 475, and **30**, 654; A. MAYER, *ibid.*, **17**, 402; P. FÜRBRINGER, *ibid.*, **17**, 526; V. LEHMANN, *ibid.*, **21**, 470, and **23**, 109; H. PASCHKIS, *ibid.*, **22**, 295; WOLFF and NEGA, *ibid.*, **26**, 116; MERGET, *ibid.*, **29**, 113; E. LUDWIG and E. ZILLNER, *ibid.*, **30**, 258; ALT, Chem. Centralbl., 1887, p. 1573; BRUGNATELLI, *ibid.*, 1889, II. p. 614.

and barium sulphate, is gently heated with aqua regia for a long time. After filtering, wash the residue with water at first mixed with some hydrochloric acid, add the washings to the filtrate, and treat the mixture with hydrogen sulphide. Should a precipitate form, examine it according to § 227. Incinerate the residue insoluble in aqua regia, fuse the ash with sodium carbonate and potassium cyanide, and treat the fused mass as directed in **302**, *β*.

c. RESIDUE III. (Compare **298**.)

The precipitate insoluble in ammonium sulphide **304**
is to be tested for the metals of Group V, according to § 229.* If a portion of the precipitate should show the presence of thallium when tested with the spectroscope, the precipitate would have to be examined for arsenic also (**299**). In this case, the arsenic goes into solution upon heating the precipitate with nitric acid, and may then be detected by means of ammonium molybdate (§ 156, 9).

d. RESIDUE IV. (Compare **299**.) **305**

This may contain tin and antimony, and perhaps also some copper. Treat it according to **123**.

9. *Examination of the Ammonium Sulphide Precipitate for Metals of Groups IV and III, especially for Zinc, Chromium, and Thallium.*†

The filtrate (**291**) from the hydrogen sulphide precipi- **306**
tate has already been mixed with ammonium sulphide. The addition of this reagent is usually attended with the formation of a precipitate consisting of iron sulphide and calcium phosphate, but it may possibly contain other metals of the third and fourth groups, especially zinc

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* Concerning the distribution of copper in the animal kingdom, and especially the detection of this metal in animal substances, compare ULEX, Zeitschr. f. analyt. Chem., **5**, 260, and **21**, 480; H. LOSSEN, *ibid.*, **5**, 261.

† With reference to the poisonous action of thallium, compare LAMY, Journ. f. prakt. Chem., **91**, 366; and for an electrolytic method of discovering thallium in chemico-legal cases, see MARMÉ, Zeitschr. f. analyt. Chem., **6**, 503.

sulphide, thallium sulphide, and chromic hydroxide, and, in addition, lead and cadmium sulphides may be present, if the precipitation with hydrogen sulphide was made in a solution which was too acid. Filter, and examine the filtrate according to **307**. Wash the precipitate with water containing ammonium sulphide, close the opening of the funnel, pour over the precipitate a mixture of 1 part of hydrochloric acid and 4 or 5 parts of hydrogen sulphide water, and allow this to stand for some time. After allowing the liquid to run off, repeat, if necessary, the treatment of any residue remaining on the filter, with hydrochloric acid and hydrogen sulphide water. If this residue points to the presence here of sulphides of metals of Group V, sufficiently dilute the solution which has run off, pass in hydrogen sulphide, filter off any resulting precipitate upon the filter which contains the residue, wash, and examine the contents of the filter for LEAD, CADMIUM, NICKEL, and COBALT. For this purpose, dissolve it by heating with dilute nitric acid, and separate any LEAD present by evaporating with an excess of dilute sulphuric acid. From the filtrate, try to precipitate any CADMIUM, by means of hydrogen sulphide, and finally separate any NICKEL or COBALT that may be present by the use of ammonium sulphide. Add ammonia to the hydrochloric acid solution (now free from lead, cadmium, nickel, and cobalt) until it is alkaline, then add yellowish ammonium sulphide, and allow the whole to stand for 24 hours at a gentle heat. If a precipitate forms, filter it off and wash it with water containing ammonium sulphide, then dissolve it in dilute hydrochloric acid, heat until the hydrogen sulphide has been expelled, filter, and add potassium iodide solution to a portion. If a pale yellow precipitate of thallious iodide were obtained, it would be necessary to precipitate the whole solution with potassium iodide. The precipitate should then be tested spectroscopically for THALLIUM. The solution containing no thallium, or no longer containing that metal, is evaporated, with the addition of some nitric acid, to a small residue, and is tested for ZINC and CHROMIUM, according to **144**.

10. *Examination of the Liquid filtered from the Ammonium Sulphide Precipitate.*

307 The fluid filtered from the precipitate produced by ammonium sulphide (306) may contain a part of, or possibly all, the chromium, as ammonia and ammonium sulphide fail to precipitate chromic hydroxide completely from solutions containing organic matter. It may also contain barium, because, if a soluble barium salt is present, Residue I would have contained only so much barium as corresponded to the sulphuric acid present in the mass or that formed by the treatment with hydrochloric acid and potassium chlorate, and the precipitate produced by hydrogen sulphide would have contained only so much as was necessary to precipitate the sulphuric acid formed by the action of the air upon the hydrogen sulphide. Finally, care demands that zinc should be taken into consideration here, since its precipitation by ammonium sulphide may have been interfered with by the decomposition products of the organic substances. Now in order to detect chromium and barium and also to test for zinc, the liquid, after the addition of a sufficient amount of dilute sulphuric acid, is evaporated, until sulphuric acid fumes escape in abundance. After cooling, dilute, filter, wash, and volatilize the sulphur filtered off. If a residue should remain here, it is to be tested for barium sulphate (208). Neutralize the sulphuric acid filtrate with sodium carbonate, evaporate to dryness, ignite the residue consisting chiefly of sodium sulphate, in order to remove ammonium sulphate, fuse the residue with sodium carbonate and potassium chlorate, test the aqueous solution of the mass for CHROMIUM, and any residue remaining, for ZINC.

11. *Testing for the State of Combination of the Metals found.*

308 If arsenic has been found in 300, or if one of the suspected metals has been disclosed upon examination of Residues I, II, III, and IV, of the ammonium sulphide pre-

cipitate, or of the liquid filtered from it, an attempt must be made to find in what combination the metal is present in the original substance. The decision of this question is always of importance, but it has especial significance in regard to those metals which are poisonous in some forms and inactive in others, as is the case, for example, with barium, which is poisonous as barium chloride or carbonate, but is inactive as barium sulphate, or in the case of chromium, which is poisonous in the form of potassium chromate, but is inactive in the form of chromic oxide.

Dialysis is generally well adapted as a means for the solution of this question. If, therefore, this operation has not been interposed between A, § 260, and C, § 262, the reserved third of the substance must be treated according to § 261, in order to obtain an appropriate solution for determining the state of combination of a suspected metal which has been found.

D. *Modifications of the process described in C.**

Of course, numerous modifications may be applied **309** to the process described in C, but a description of these can be omitted here, because all the circumstances under which they might possibly offer advantages in comparison with the methods described cannot be foreseen. But attention must be called to two modifications which relate to a different manner of producing metallic arsenic.

1. While the course prescribed in **300** requires portions of the weighed sulphide of arsenic to be reduced by fusing with sodium carbonate and potassium cyanide, J. Otto and Rob. Otto† recommend subjecting to

* In regard to the separation of arsenic by distillation as arsenious chloride, according to the method originally given by Schneider and by Fyfe, compare Selmi, Ber. d. deutsch. chem. Gesellsch., **5**, 289, and Zeitschr. f. analyt. Chem., **21**, 307; H. Hager, Pharmac. Centralhalle, 1881, p. 169; J. A. Kaiser, Zeitschr. f. analyt. Chem., **14**, 250, and **22**, 478; E. Fischer, *ibid.*, **21**, 266; Hufschmidt, *ibid.*, **24**, 255; Beckurts, Pharmac. Centralhalle, 1884, p. 488; Ambühl, Chem. Centralbl., 1892, I, p. 456. Concerning other methods, see also C. H. Wolff, Zeitschr. f. analyt. Chem., **27**, 125; v. Itallie, Chem. Centralbl., 1890, I, p. 361; J. Clark, *ibid.*, 1893, II, p. 148.

† F. J. Otto's "Anleit zur Ausmittelung der Gifte," sechste Aufl., von Rob. Otto, p. 190.

the reduction by potassium cyanide, not arsenious sulphide, but the arsenic acid produced from it. For this purpose, put concentrated nitric acid upon the sulphide of arsenic contained in a dish, evaporate, repeat the operation if necessary, remove every trace of nitric acid by repeatedly moistening the residue with water, and drying; soften the residue with a few drops of water, add pulverized sodium carbonate so that an alkaline mass is formed, and completely dry this in the dish, with frequent stirring, taking care to bring it into the middle of the dish in as small a space as possible. This mass is then very well adapted for reduction, but in this process, it is necessary that the residue should be free from *every trace* of nitric acid or nitrates; otherwise deflagration would take place upon igniting with potassium cyanide, and the experiment would fail.

2. Instead of precipitating the solution obtained in 299 with hydrogen sulphide, it may be also tested directly in MARSH'S apparatus, in the manner described in § 155, 10.* If arsenic is present in any considerable quantity, only a part of the previously measured or weighed liquid will suffice to obtain distinct arsenic mirrors, and the rest may then be used for the quantitative determination of the arsenic. But if only minute amounts of arsenic are present, so that, adding it little by little, one is compelled to add the whole amount of the liquid to the MARSH'S apparatus in order to obtain a distinct mirror of arsenic, a quantitative determination must be abandoned.† In order not to lose any of the arsenic which escapes as hydrogen arsenide, it is advisable to lead the gas which passes out of the heated tube into a solution of silver nitrate acidified with nitric acid (§ 157, 7).

In the process described, the importance of using

* The reduction of arsenic acid with sulphurous acid is not necessary in this case.

† [See, however, a method for weighing the arsenical mirror, JOHNSON and CHITTENDEN, Am. Chem. Jour., 2, 235, and 5, 8.] According to F. W. SCHMIDT, it is possible to expel all the arsenic from the evolution-flask if stannous chloride is added to it (Chem. Centralbl., 1892, II, p. 306). [According to JOHNSON and CHITTENDEN, the operation is quantitative under the proper conditions without any such addition.]

zinc which is absolutely free from arsenic, has been already explained in § 155, 10. It should be added here, that for legal investigations, use should be made of only such zinc as is free from sulphide, and only such as does not yield the slightest arsenical coating, in a properly heated glass tube, in the apparatus described in § 155, 10, when a quantity of it equal to that to be used for the legal experiment is completely dissolved in the pure sulphuric acid which is also to be used for the actual experiment. In consideration of the fact that nearly all the glass tubing to be found at the present time contains arsenic, it will be an act of caution if a part of the tube to be used for the actual test is taken to test the zinc and sulphuric acid. For a confirmation of the fact that the mirror obtained is actually an arsenical mirror, if this is considered necessary, the treatment of the mirror with hydrogen sulphide, etc., should be chosen. (Compare § 155, 10).

II. Method for the Detection of Hydrocyanic Acid.

§ 263.

If there has occurred an actual or probable case of 310
poisoning with hydrocyanic acid or with potassium cyanide (which acts similarly to hydrocyanic acid, and is easier to obtain, because it is extensively used in the arts), and if hydrocyanic acid is to be separated from food or the contents of a stomach and detected, it is absolutely necessary to act quickly; in the first place, because hydrocyanic acid, being an easily decomposable body, may otherwise be lost,* but also for the additional rea-

* The decomposition of hydrocyanic acid takes place sometimes more rapidly, sometimes more slowly, but generally a rather long time intervenes before *all* the hydrocyanic acid which has entered into the organism is decomposed. In relation to experiments made in regard to this question, compare Dragendorff, "Die gerichtlich chemische Ermittelung von Giften," 3. Aufl. Göttingen (Vandenhöck & Ruprecht), 1888, p. 59; Buchner, Journ. f. prakt. Chem., **104**, 338; Bonjean, Pharmac. Centralhalle, 1871, p. 199; H. Struve, Zeitschr. f. analyt. Chem., **12**, 14 and 19; Rennard, *ibid.*, **13**, 110; Reichard, Arch. d. Pharm., **219**, 204; Sokoloff, Zeitschr. f. analyt. Chem., **14**, 423.

son (at least in the opinion of some investigators) that cyanogen compounds may be formed in the process of putrefaction of animal substances, a view which certainly cannot be regarded as surely demonstrated.* If a dead body is under investigation, there are taken into consideration, besides the stomach and the intestinal canal, the blood, the brain, the liver, and also the urine.

In addition to the poisonous cyanogen compounds, among which hydrocyanic acid and potassium cyanide take the first place, there are those which are not poisonous, among which potassium ferrocyanide and ferricyanide, and also Prussian blue, are the best known. By the action of even weak acids upon the latter, a part of their cyanogen is converted into hydrocyanic acid, and therefore some preliminary experiments are first necessary in order to decide which method should be chosen for the separation of hydrocyanic acid, so that a safe conclusion may be drawn concerning the original presence of this acid or of potassium cyanide.

A. Preliminary Experiments.

1. Test the odor of the substance to be investigated. 311
Hydrocyanic acid, if present in any considerable amount in substances free from bodies with other odors, is to be recognized at once. However, if the parts of the body to be tested have already begun to putrefy, the hydrocyanic acid odor may be completely hidden by the odor of the decaying substances. The odor alone, however, can never be considered sufficient proof of the presence of hydrocyanic acid, for benzaldehyde and nitrobenzol have somewhat similar odors.

2. Place some of the substance, after the addition of 312
water, if necessary, upon a moistened filter, allow some of the liquid to run through, acidify this with hydrochloric acid, and test with ferric chloride for ferrocyanogen, and

* In reference to this question, compare Taylor in Dragendorff, *op. cit.*, p. 59; Bonjean, Pharmac. Centralhalle, 1871, p. 199; W. Preyer, Zeitschr. f. analyt. Chem., 12, 23.

with ferrous sulphate for ferricyanogen. In the first test, the presence of soluble sulphocyanides would be recognized. If Prussian blue were present in the substance to be investigated, it would generally reveal itself by its color. If a ferrocyanogen, ferricyanogen, or sulphocyanogen compound is found, the detection of any simple cyanogen compounds (hydrocyanic acid or potassium cyanide) in the presence of these requires the greatest care. Pass on to B, 2.*

3. If ferrocyanogen, ferricyanogen or sulphocy- 313
anogen compounds have not been found, proceed to test with cupriferous guaiacum-paper. In the next place, test the reaction of the substance, which, if not liquid, is to be mixed with some water. If the reaction is acid, the substance is fit for direct testing; if it is neutral or alkaline, exactly acidify it with tartaric acid solution. Then test the air in the vessel over the substance under investigation, by hanging in it a guaiacum-paper containing copper, according to § 185, 10. If the paper becomes blue, this is not an absolute proof, but a very marked indication, that hydrocyanic acid or potassium cyanide is present. Any mercuric cyanide present would not give the reaction. Pass on to B, 1 (315).

4. If the preliminary tests in 1, 2, and 3, have given 314
negative results, mercuric cyanide might still be present. Pass on to B, 3 (320).

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* Potassium ferrocyanide and ferricyanide decompose even in cold aqueous solutions, and more abundantly and more quickly in acid or warm solutions; hence if hydrocyanic acid is found in a dead body in the presence of ferro- or ferricyanogen compounds, ALMÉN (Chem. Centralbl., 1872, p. 439) believes that a conclusion can never be drawn that poisoning has occurred with hydrocyanic acid or potassium cyanide, and, according to my opinion, such a conclusion can be drawn only under certain conditions, *e.g.*, when there is found in a body soon after death a relatively large quantity of hydrocyanic acid with little potassium ferrocyanide. (Compare also LUDWIG and MAUTHNER, Zeitschr. f. analyt. Chem., 20, 604.)

B. The Separation and Detection of Hydrocyanic Acid or of Cyanogen in Poisonous Cyanides.

315 1. If the preliminary examination (A, 2) has shown the absence of ferrocyanogen, ferricyanogen, and sulphocyanogen compounds, and if the guaiacum-paper has turned blue (A, 3), mix the substance to be investigated, with water if necessary, add solution of tartaric acid until it reddens litmus-paper strongly (if it does not already react strongly acid), introduce the mixture into a retort, which is so arranged that its body is placed in an iron or copper vessel without touching the bottom of the latter, and, for the sake of safety, the bottom of the vessel is covered with a cloth. The metallic vessel is then filled with calcium chloride solution or with paraffine oil, and is cautiously heated, so that the contents of the retort, the neck of which slants upwards, are brought to gentle boiling. With the aid of a tight-fitting tube bent at an obtuse angle, conduct the vapors passing over through a condenser,* and receive the distillate in a small, graduated cylinder or a tared flask. The mouth of either of these should be closed with a doubly perforated stopper. The cooling-tube of the distilling-apparatus passes through one of the holes of the stopper, while the other is provided with a glass tube, bent twice at right angles, which leads into a U-tube containing some very dilute sodium hydroxide solution (which is certainly free from sodium cyanide). As soon as about 12 cc have been distilled over, the small cylinder or the flask is removed, and is replaced by a larger graduated cylinder or tared flask, which is also to be connected with the U-tube.

316 Measure or weigh the first distillate, and test it as follows:

a. Treat a quarter of it according to § 185, 7, in order to convert the hydrocyanic acid into the form

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*In testing for phosphorus at the same time, the condenser must be entirely of glass, and the operation must be conducted in a perfectly dark room. (Compare § 264.)

of ferric sulphocyanide. Since the distillate may easily contain acetic acid, do not neglect to add somewhat more hydrochloric acid at last, in order to counteract the injurious influence of any ammonium acetate.

b. Treat another quarter according to § 185, 6, in order to convert the cyanogen of the hydrocyanic acid into the form of Prussian blue.

c. If the presence of hydrocyanic acid has been shown with certainty in experiments *a* and *b*, use the half of the distillate still remaining for an approximate quantitative determination. But if only one of the two reactions has now given an entirely certain result, use another quarter of the distillate for the reaction described in § 185, 8, depending upon the conversion of the hydrocyanic acid into potassium nitroprusside, and then use the last quarter for the quantitative determination.

d. In order to carry out the approximate quantitative determination, continue the distillation as long as a liquid containing hydrocyanic acid passes over, mix this distillate with the contents of the U-tube, take one half, or, as the case may be, one quarter, of this liquid, and unite it to the corresponding half or quarter remaining of the first distillate. If the liquid should not react acid already, add a little tartaric acid to acid reaction, introduce it into a retort, add borax or sodium bicarbonate in order to hold back hydrochloric acid, and distil to a small residue. This distillate contains all the hydrocyanic acid and is free from hydrochloric acid. Now add silver nitrate to it, then ammonia until this is in excess, and finally nitric acid to strongly acid reaction. Allow the resulting precipitate to settle, filter upon a filter which has been dried at 100° and weighed, wash, dry completely at 100°, and weigh the silver cyanide obtained. This weight, multiplied by .2018, gives the corresponding amount of anhydrous hydrocyanic acid, and this result multiplied by 2 or, if the case requires it,

by 4 (since only one half or one fourth was used for the determination), gives the whole quantity of hydrocyanic acid that was present or was formed by the decomposition of potassium cyanide.

2. If the preliminary tests have shown the presence 317
of ferro-, ferri-, or sulphocyanogen, the method described in 1 (315) for the separation of hydrocyanic acid cannot be used. One of the following methods must therefore be substituted :

a. METHOD WHICH IS SUITABLE IN THE PRESENCE OF FERRO-, FERRI-, OR SULPHOCYANOGEN. If necessary, add water to the object to be tested, then tartaric acid, and finally add sodium carbonate by degrees, to slightly alkaline reaction. Treat the mixture in a stream of carbon dioxide at a temperature not exceeding 60°, in the distilling-apparatus described in 315, and proceed with the distillate according to 316.* The statement that the temperature of the distillation is not to exceed 60° is based upon HILGER and TAMBA's experiments.

b. METHODS WHICH ARE SUITABLE FOR COUNTERACTING THE INTERFERENCE OF FERRO- AND FERRICYANOGEN COMPOUNDS, BUT NOT THAT OF SULPHOCYANOGEN COMPOUNDS.

α. If necessary, dilute the substance under 318
investigation with water, acidify it slightly with hydrochloric acid, and add ferric chloride if potassium ferrocyanide was present, or ferrous sulphate if potassium ferricyanide was present, using a slight excess in either case. Saturate the liquid with sodium chloride, filter off the precipitate, and proceed with the filtrate, now freed from ferro- and ferricyanogen, according to 1 (315).†

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* JAQUEMIN, Ann. Chim. Phys. (5), 4, 135; BECKURTS and SCHÖNFELD, Arch. f. Pharmacie, 21, 576, Zeitschr. f. analyt. Chem., 23, 116; F. J. OTTO, "Ausmittelung der Gifte," 6te Aufl., von R. OTTO, p. 34; TAYLOR, Zeitschr. f. analyt. Chem., 24, 259; H. STRUVE *ibid.*, 12, 24; A. HILGER and K. TAMBA, *ibid.*, 30, 529; W. AUTENRIETH. Chem. Centralbl., 1893, I, p. 773.

† V. PÖLLNITZ, DRAGENDORFF, ALMÉN, Chem. Centralbl., 1872, p. 429; LUDWIG and MAUTHNER, Zeitschr. f. analyt. Chem., 20, 604.

If the precipitate cannot be separated from the liquid, pass a stream of air through the latter at the ordinary temperature, in a flask, after having precipitated with ferric chloride or ferrous sulphate, and pass this air through a weak solution of sodium hydroxide which is certainly free from sodium cyanide, and then subject portions of this to tests for sodium cyanide (and consequently for hydrocyanic acid), according to § 185, 6, 7, and 8. The amount of cyanogen in the remainder of the alkaline liquid is then to be determined, as in 1.

β. If necessary, dilute the substance to be 319
examined, with water, then acidify slightly with tartaric acid, and shake thoroughly with an equal volume of ether. After removing the layer of ether, repeat the extraction. The united ether extracts are free from hydroferro- and hydroferricyanic acids, but they contain the hydrocyanic acid originally present, and also that which has been liberated from potassium cyanide. The free hydrocyanic acid may now be removed from the ethereal extract by shaking with water containing sodium hydroxide, and it may be determined in the latter, as in 2, *b*, *α* (318).*

In the presence of mercuric cyanide, this method is to be less highly recommended, because, although this salt does go into the ethereal solution when its aqueous solution is shaken with ether, still this takes place only in moderate amount, and completely only with difficulty.

3. In order that any cyanogen present in the form of 320
mercuric cyanide may not be overlooked, mix the substance to be tested with tartaric acid to strong acid reaction, add sodium chloride, heat in the distilling-apparatus described in 315, and proceed with the distillates, and with the dilute sodium hydroxide placed in front in the U-tube, as in 316.†

* Barfoed, Beckurts, and Schönfeld, Zeitschr. f. analyt. Chem., 23, 117.

† Concerning other methods for separating the cyanogen from mercuric cyanide, compare Vitali, Chem. Centralbl., 1889, II, p. 392.

III. Method for the Detection of Phosphorus.*

§ 264.

Since phosphorus paste has been employed to poison 321
mice, etc., and the poisonous action of matches prepared with colorless phosphorus has become extensively known, this agent has not infrequently been resorted to as a means for committing murder. The chemist is therefore occasionally called upon to examine some article of food, or the contents of a stomach, for this substance. In cases of the kind, it is obvious that the whole attention of the analyst must be directed to the separation of the phosphorus in the *free state*, or to the production of such reactions as will enable him to infer the presence of *free phosphorus*. The mere finding of phosphorus in the form of phosphates would prove nothing, for phosphates invariably form constituents of animal and vegetable bodies.

By the action of the air, free phosphorus, when present, first changes into phosphorous acid and finally into phosphoric acid (which no longer permits the conclusion that free phosphorus has originally been present), and hence all unnecessary delay must be avoided. However, since particles of phosphorus which are enclosed by slimy organic matter last for a rather long time before they are completely oxidized to phosphoric acid, the detection of free phosphorus in the parts of a dead body often succeeds, even when the latter are examined several weeks after death has taken place.† The certainty of the results of some of the methods to be immediately described may be interfered with, however, by the fact shown by the repeated experience of Selmi,‡ that in the putrefaction of

* Since only colorless phosphorus, and not the red modification, is poisonous, by "phosphorous" in what follows, the poisonous, colorless phosphorus is always to be understood.

† Neumann, Taylor-Seideler, "Gifte," II, 179; Dragendorff, "Ermittelung von Giften," 3te Aufl., p. 99; Fischer and Jul. Müller, Zeitschr. f. analyt. Chem., 15, 57; Elvers, Chem. Centralbl., 1877, p. 70; Medicus, Zeitschr. f. analyt. Chem., 19, 164.

‡ Ber. d. deutsch. chem. Gesellsch., 9, 1127, and 11, 1691.

albumen, brain-matter, and even of parts of the body preserved in alcohol, especially the intestines, volatile substances containing phosphorus may be easily formed, which are soluble in ether and carbon disulphide, and turn a solution of silver nitrate brown.

In the examination of dead bodies, in addition to the stomach and intestines, the liver, brain,* blood, and urine † should be taken into consideration.

A. *Detection of Unoxidized Phosphorus.*

1. Preliminary Testing.

a. In the first place, ascertain whether the presence **322** of unoxidized phosphorus in the substance under investigation is indicated by its smell, or by its luminosity in the dark.‡ To this end, take care to increase the contact of the phosphorus with the air, by rubbing, stirring, or shaking.

b. Put a little of the substance (as proposed by J. **323** Scherer§) into a small flask, fasten to the loosely inserted cork a strip of filtering-paper moistened with neutral solution of silver nitrate, and heat to 30° or 40°. If the paper does not turn black, even after some time, no unoxidized phosphorus is present, and it is consequently hardly necessary to apply the methods given in 2, but the operator may at once pass on to **336**. If, on the other hand, the paper turns black, this is no positive proof of the presence of phosphorus, as hydrogen sulphide (to be

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* Since the brain is phosphorescent in itself, and since putrefied brain-matter, when distilled with water, always yields a distillate containing phosphorus, it is recommended to carry out the examination of the brain separately.

† In regard to the peculiar properties and to the unusual behavior which the urine shows after phosphorus poisoning, compare Selmi, Zeitschr. f. analyt. Chem., **14**, 232, and **21**, 481; v. Mehring, *ibid.*, **15**, 507; Pesci and Stroppo, Pharmac. Centralhalle, 1880, p. 166.

‡ Attention is here called to the fact that luminescence in the dark does not permit the certain conclusion that phosphorus is present, because there are many other causes of such phenomena of phosphorescence.

§ Ann. d. Chem. u. Pharm., **112**, 214.

detected with a strip of paper moistened with lead solution or with antimonious chloride), formic acid, putrefying matters, etc., may also cause blackening of the paper. Treat, therefore, the principal mass of the substance by methods *a* and *b* in 2, or also according to one of the other methods mentioned in 2.

2. Actual Examination.

a. By distillation with water.

This excellent and approved method, recommended by E. Mitscherlich,* is based upon driving off the phosphorus with water-vapor, and causing it to phosphoresce. 324

Mix a considerable portion of the substance to be tested, with water and some dilute sulphuric acid,† or (if testing for hydrocyanic acid at the same time) tartaric acid, and subject the mixture to distillation in the flask *A* (Fig. 47), the contents of which are heated to gentle boiling and kept so, most safely in a bath of liquid paraffine. Connect the flask with the delivery-tube *bb*, and this with the glass cooling-tube *dd*, which passes through the larger glass cylinder, and is fastened into it by means of rubber stoppers. The cooling-tube opens into the flask *c*. Cold water is conducted from the cock *a* into the funnel-tube *c*, and the warmed cooling-water flows off through *e*.

Now if the substance in *A* contains phosphorus, there will appear, in the dark, at the place where the steam enters the cooled part of the tube at the top, a strong luminosity, usually a luminous ring, which moves up and down. If 150 g of a mass containing only 1.5 mg of

* Journ. f. prakt. Chem., **66**, 238.

† If it is supposed that the phosphorus has been introduced into the substance under investigation in the form of phosphorus matches, H. Hager (Zeitschr. f. analyt. Chem., **10**, 255) recommends the further addition of some ferrous chloride or sulphate, in order to render harmless the oxidizing substances present in the matches. If a reaction for hydrogen sulphide has been obtained in the preliminary examination 323, then ferric chloride must be added to the substance to be distilled, in order to prevent the appearance of hydrogen sulphide in the distillate.

phosphorus, and accordingly only 1 part in 100,000, is taken for distillation, 90 g may be distilled over (taking more than half an hour) without the luminosity ceasing. In making the experiment, MITSCHERLICH stopped the distillation after half an hour, allowed the flask to stand

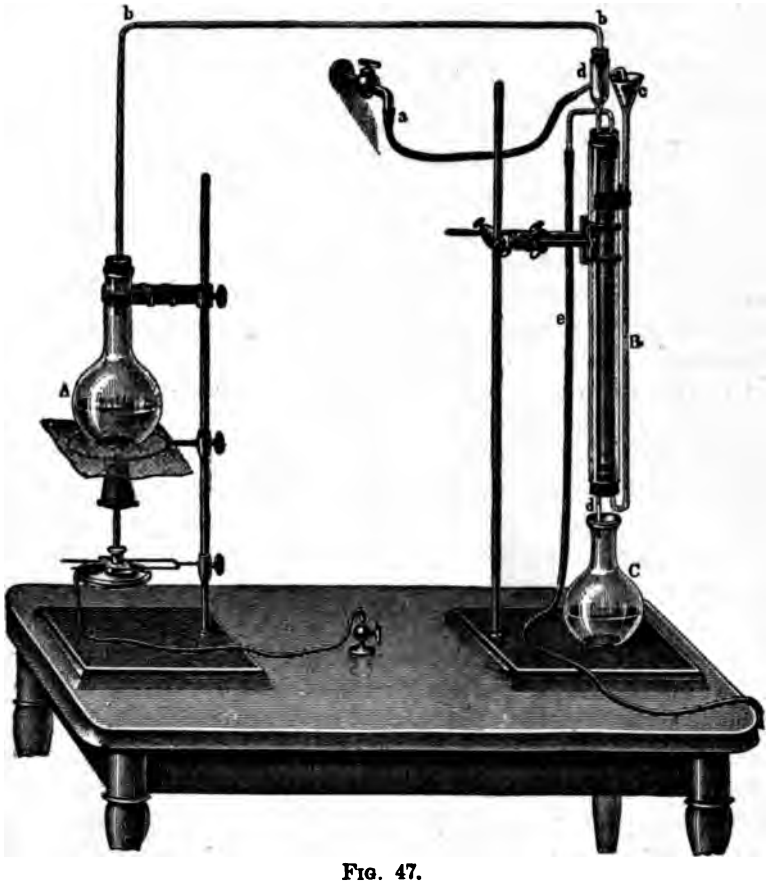

FIG. 47.

uncorked for a fortnight, and then recommenced the distillation, when the luminosity was as strong as at first. Instead of the cooling-apparatus shown, an ordinary condenser, placed in a slanting position, may be used, provided that it is made entirely of glass. A cooling-apparatus of different form is recommended by H. HAGER.*

* Pharmac. Centralhalle, 1870, p. 465, Zeitschr. f. analyt. Chem., 10, 255.

If the fluid contains substances which prevent the lu- 325
minosity of phosphorus (such as ether, alcohol, benzine, phenol, petroleum-ether, or oil of turpentine, and many other ethereal oils), no luminosity is observed as long as these substances continue to distil over. In the case of ether and alcohol, however, this is soon finished, and the luminosity very speedily makes its appearance. Oil of turpentine and other ethereal oils, on the other hand, prevent the luminosity permanently, but free sulphur does not prevent it. Hydrogen sulphide, however, in case it is present or is formed by acidifying the mass under investigation, must be decomposed, as already mentioned, by the addition of some ferric chloride before beginning to heat. Sulphurous acid, chlorine, mercuric chloride, and, in case the solution is only weakly acidified, even cupric sulphate, prevent the luminosity (BERNBECK).

At the bottom of the flask into which the distillate flows, globules of phosphorus are found, if any considerable amount of it is present. From 150 g of a mixture containing .02 g of phosphorus, MITSCHERLICH obtained so many globules of that body that the tenth part of them would have been sufficient to demonstrate its presence. In medico-legal investigations, these globules should be washed with alcohol, and then weighed. Afterwards a portion may be subjected to confirmatory examination, to make quite sure that the globules really consist of phosphorus; while the remainder, together with a portion of the fluid, which shows the luminosity upon distillation, should be sent in with the report.

The operation should be conducted in an entirely dark place, best at night. When it is performed in the daytime, care should be taken to shut out all light, as where this is not effectively done, the rays entering through some chink or crevice may chance to be reflected by the glass vessel or by the fluids, and thus lead to deception. It is advisable to pass the horizontal part of the evolution-tube *b* through the aperture of a screen, to guard effectively against reflection of light from the lamp. These precautionary measures are of

course necessary only where very minute traces of phosphorus are to be detected.

The residue left in the distilling-flask is then exam- 326
ined for phosphorous acid as directed in 336. The distillate may also be examined in the same way, to confirm the presence of phosphorus, or to show the presence of phosphorous acid formed by the oxidation of phosphorus fumes.* But if this is to be used for a determination of the phosphorus which was present in the free state (a determination which is admittedly only a mere approximation), after the distillation has been continued until the phosphorescence has ceased, treat the whole of the contents of the receiver with chlorine, in order to convert all the phosphorus and all the phosphorous acid into phosphoric acid; determine this, after proper concentration, by precipitating with magnesium mixture, and double the amount of phosphorus contained in the phosphoric acid which is found. In this way, too small, rather than too great, an amount of phosphorus is often found.†

If the character of the mass to be tested for phos- 327
phorus causes fear that the liquid may bump upon boiling, it is advisable to conduct the distillation in a flask heated upon a sand-bath, and into it pass steam under moderate pressure. If the apparatus is first filled with carbon dioxide, and if the distillation with steam is continued for a sufficient length of time, almost the

* If a mass which at the same time contains hydrocyanic acid and phosphorus is distilled, the former is found most advantageously in the distillate which goes over at first, the latter in the distillate coming over afterwards. Take care, therefore, in any case, to change the receiver after about 15 cc have gone over, in order to obtain any hydrocyanic acid in a sufficiently concentrated condition, and do not omit to connect the receiver with a U-tube containing dilute sodium hydroxide solution. (Compare 315.)

† If an apparatus which is not unnecessarily large is selected for the distillation, and the operation is conducted in such a manner that the luminescence appears in the cooling-tube and not in the flask or in the tube connected with the condenser, and the operation is continued until no more phosphorescence appears, even in a totally dark room, at least one half, and under especially favorable conditions, as much as three quarters of the phosphorus which was present in the free state is obtained (LOTH. MEYER, O. SCHIFFERDECKER, Zeitschr. f. analyt. Chem., 11, 279).

whole amount of the free phosphorus is found in the distillate (M. BUCHNER*).

It is to be noted that the mere detection of phosphoric acid in the distillate treated with chlorine is no certain proof of the presence of free phosphorus in the substance under investigation, even if one does not admit the possibility that small amounts of the phosphoric acid present may pass over into the distillate by spattering. (Compare the results obtained by SELMI, mentioned in 321, and also the experience of H. W. BETTINK and E. v. EMBDEN,† who, from parts of the body of a man who had used hypophosphites as a medicine, obtained distillates in which hypophosphorous acid and hydrogen phosphide were detected.)

b. BY EXPELLING PHOSPHORUS IN A CURRENT OF CARBON DIOXIDE.

In the method described under *a*, the phosphorescence 328
is prevented by the presence of many substances; hence it is always advisable to treat a further portion of the substance under investigation according to the following method, which was originated by NEUBAUER and myself:‡ Put the substance, with addition of water if necessary, into a flask with a doubly perforated stopper, add dilute sulphuric acid to acid reaction, conduct washed carbon dioxide (evolved from a KIPP'S apparatus, p. 289) in a slow stream into the flask, by means of a glass tube reaching nearly to the bottom, and let the gas, issuing from another glass tube inserted into the other perforation of the cork, pass through one or two U-tubes containing a neutral solution of silver nitrate. When the flask is filled with carbon dioxide, heat it on the water-bath. Continue the operation for several hours. If free phosphorus is present, it will volatilize unoxidized in the stream of carbon dioxide, then pass into the

* Zeitschr. f. analyt. Chem., 14, 165.
† Chem. Centralbl. 1893, II. p. 1104.
‡ Zeitschr. f. analyt. Chem., 1, 336.

silver solution, where it will form insoluble, black silver phosphide on the one hand and metallic silver on the other hand. The formation of a precipitate is not sufficient proof of the presence of phosphorus, as the precipitate may owe its formation to volatile reducing agents or to hydrogen sulphide, but if a precipitate does not form, it is safe to conclude that unoxidized phosphorus is absent.

If a precipitate has formed, however, filter through a 329
filter well washed with dilute nitric acid and water, and wash it with water. The presence of silver phosphide in it may be shown by BLONDLOT'S improved modification of DUSART'S method,* best by substituting for the ap-

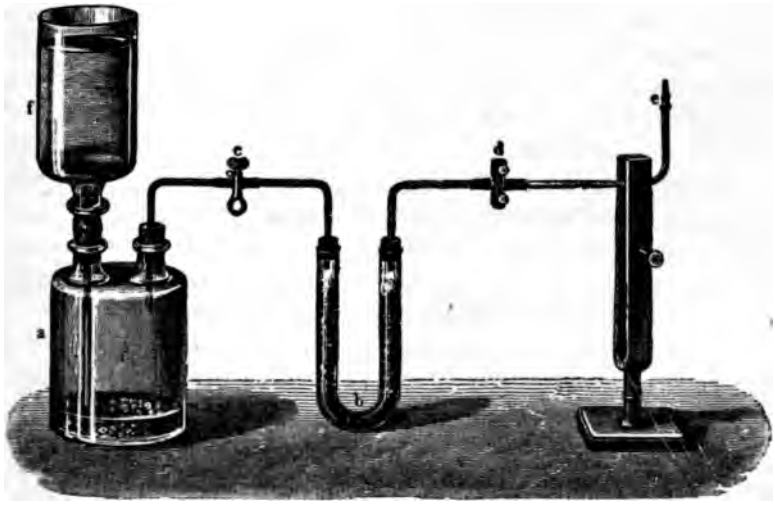

FIG. 48.

paratus used by BLONDLOT, the one shown in Fig. 48, which may be easily constructed.

a is a hydrogen evolution-bottle; *b* contains pumice stone moistened with concentrated solution of caustic potash (for the purpose of holding back any hydrogen

* Zeitschr. f. analyt. Chem., 1, 129. According to BLONDLOT, the organic substances to be tested for phosphorus are treated directly (a procedure which is not to be recommended) with zinc and sulphuric acid, and the evolved gas is passed into silver solution.

sulphide, as this interferes with the reaction); *c* is a common pinch-cock; *d* is a screw pinch-cock; and *e* is a platinum jet, which is kept cool by tying moistened cotton round it. This platinum jet is indispensable to the production of a colorless hydrogen flame, as the soda in glass will always color the flame yellow.*

To ascertain whether the zinc and sulphuric acid will give a gas quite free from hydrogen phosphide, let the evolution go on a short time, then close *c* until the fluid has ascended from *a* to *f*. Close *d*, open *c*, and regulate *d* by means of the screws, so as to obtain a suitable flame. If the flame, viewed in a dark place, is colorless, showing no trace of a green cone in the center, and no emerald-green coloration when allowed to play upon a porcelain surface, as in MARSH'S experiment, the hydrogen may be considered pure. It is advisable to repeat the experiment. Rinse the precipitate under examination into *f*, take care that every particle of it reaches *a*, then repeat the experiment. If the precipitate contains even a minute trace of silver phosphide, the green cone in the center of the flame and the emerald-green coloration will now become distinctly visible.

Remove the excess of silver from the solution filtered 330
from the silver precipitate, by hydrochloric acid, pass through a filter well washed with acid and water, remove the hydrochloric acid by repeated evaporation with nitric acid on the water-bath, take up with a little nitric acid, and test for phosphoric acid with molybdic acid solution, or with a mixture of magnesium sulphate, ammonium chloride, and ammonia.

By this method, we obtained the clearest evidence of the presence of phosphorus in a large quantity of putrid blood mixed with the head of a common match containing colorless phosphorus; and this even in presence of substances which prevent the luminosity of the phosphorus in MITSCHERLICH'S method. The appearance of the green flame and the detection of phosphoric acid in the liquid

* In relation to burning hydrogen which contains phosphorus in such a manner that a platinum tip may be dispensed with, see 332.

filtered from the silver phosphide has not, however, the same demonstrative force as the appearance of phosphorescence in MITSCHERLICH'S method, or at least it has not that value in the examination of putrefied parts of dead bodies. (Compare the results of SELMI, mentioned in **321**, and those of J. V. D. HAGEN and P. WOLTERING.*)

If there is sufficient phosphorus present to permit a **331** quantitative determination, it is best to use SCHERER'S more accurate modification of MITSCHERLICH'S process,† since the method given in **326** gives only a very approximate result. This is effected by distilling another portion of the mass, acidified with sulphuric acid, with the addition, if required, of ferrous sulphate (compare the last foot-note on p. 612) in an atmosphere of carbon dioxide. With respect to this, I would suggest that it is best to provide the distilling-flask with a doubly perforated stopper and to transmit pure carbon dioxide until the apparatus is filled with it, but then to shut off the gas stream. A flask with a doubly perforated cork serves for a receiver; while the end of the condensing-tube passes into one of the openings, and into the other is inserted a bent glass tube, which leads to a U-tube containing a solution of pure silver nitrate.

When the distillation is over, globules of phosphorus are found in the receiver. A moderate stream of carbon dioxide is now once more transmitted through the apparatus, and a gentle heat applied, with a view to effect the formation of larger globules by aggregation. These are then washed and weighed as in MITSCHERLICH'S method. The fluid poured off from the phosphorus globules is luminous in the dark when shaken. It requires, however, a larger proportion of phosphorus to obtain distinct luminosity in this way than is the case in distilling with steam (**324**). The phosphorus in the fluid, after oxidation by nitric acid or chlorine, may be determined as phosphoric acid. To obtain the remainder of the phosphorus, treat the contents of the U-tube with nitric acid, throw down the silver by hydrochloric acid, filter through a washed

* Chem. Centralbl., 1893, II, p. 1103.
† Ann. d. Chem. u. Pharm., 112, 216.

filter, concentrate in a porcelain dish, precipitate the phosphoric acid as ammonium magnesium phosphate, and weigh it as magnesium pyrophosphate. The phosphoric acid obtained from the liquid or from the contents of the U-tube, however, can only be considered as having come from free phosphorus originally present, unless no particles of the distilled liquid have spattered over, and unless the substance under examination was free from putrefying brain-matter, etc. (Compare 321.)

c. By expelling phosphorus in a current of hydrogen.

332 Since the mixing of the substance under investigation with zinc and sulphuric acid, according to Blondlot, renders the further examination of the residue containing zinc for other poisons more difficult, Dalmon* passes pure hydrogen gas directly through the organic substance containing phosphorus, and under these circumstances, the gas takes up phosphorus. He allows the gas to escape from a tube bent at right angles and properly drawn out, and places over the flame a sufficiently long but narrow glass tube, after the manner of the "chemical harmonica." The flame then contracts, without giving a sound, and appears green throughout its whole extent. If the tube in which the hydrogen containing phosphorus was burnt is rinsed out with a little water, the phosphoric acid produced in it may be detected with molybdenum solution. Neubauer,† who has confirmed Dalmon's statements, calls attention to the fact that, in addition, the escaping hydrogen containing phosphorus, when not ignited, shows a beautiful phosphorescence in a dark room.

d. By distilling with alcohol.

333 If the substance to be examined is received immersed in alcohol, the following method proposed by H. Hager‡

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* Journ. de Chim. médicale, 1870, p. 123.

† Zeitschr. f. analyt. Chem., 10, 132.

‡ Pharmac. Centralhalle, 1870, p. 455; Zeitschr. f. analyt. Chem., 10, 256.

is to be recommended: After the addition of some sulphuric acid, and, if there is cause to suppose that the phosphorus comes from phosphorus matches, some ferrous chloride also, distil off the alcohol, using a water-bath. No luminescence is produced here, but the distillate is alcohol containing phosphorus. If the distillation is repeated, with the addition of more alcohol, it is possible to collect small quantities of phosphorus completely in the distillate. If a test-tube which is one third full of water is taken, and about ten drops of the phosphoriferous alcohol are added, especially that which came over first, and shaken in the dark, the whole tube appears filled with phosphorescent light. The alcohol containing phosphorus becomes brown or black with a solution of silver nitrate, or also with cupric sulphate solution, with the separation of metallic phosphides and metals, and with the formation of phosphoric acid. It is easy to test with lead-paper, to find whether hydrogen sulphide was not possibly the cause of the reaction.

e. By extraction with solvents which do not mix with water.

334 If liquid solvents of phosphorus which do not mix with water are shaken with organic substances containing free phosphorus, suspended in water, the phosphorus is taken up by the solvents, and remains behind upon their careful evaporation. It is advisable to add a little water here, in order to protect the phosphorus from the oxidizing action of the air after the volatilization of the solvent. As appropriate solvents for this purpose, there have been proposed, carbon disulphide by Selmi,* ether by Lassaigne† and by van Bastelaer,‡ and petroleum-ether by H. Hager.§ When the solvents have been almost wholly removed by spontaneous evaporation, at the ordinary temperature, the residues generally show phosphor-

* Ber. d. deutsch chem. Gesellsch., 5, 289.
† Pharm. Centralbl., 1850, p. 360.
‡ Zeitschr. f. analyt. Chem., 13, 350.
§ *Ibid.*, 20, 321.

escence at once in the dark, when poured out upon a flat plate. Moreover, they may be tested by the methods already mentioned. For the purpose of obtaining phosphorus as pure as possible in the extraction of mixtures containing fats, VAN BASTELAER recommends the following process: After the evaporation of the ether in the presence of some water, heat the residue to 50° or 60°, treat the fat thus fused, containing the phosphorus, by shaking it repeatedly with concentrated aqueous ammonia, in order to dissolve it, and wash the phosphorus, which is scarcely attacked by this operation, first with water containing sulphuric acid, and then with pure water.

DUSART'S method* (in which the substance under investigation is extracted with a mixture of equal volumes of carbon disulphide, ether, and alcohol, containing sulphur in solution, after the evaporation of which sulphur containing phosphorus is obtained) is closely related in this respect to the methods of LIPOWITZ† and E. MULDER,‡ but it varies from the latter methods, in the manner in which phosphoriferous sulphur is further treated. In relation to the details of these less-used methods, I refer to the original articles. 335

B. *Detection of Phosphorous Acid.*

Should all attempts to detect phosphorus, as such, fail, find whether it may not be possible to detect the first product of its oxidation, *i.e.*, phosphorous acid. For this purpose, transfer the residue left in **326**, or that of **328**, or **331**, to the apparatus charged and tested as in **329** and illustrated by Fig. 48, p. 617, and observe whether the coloration of the hydrogen flame reveals the presence of phosphorus (WÖHLER). Should this be the case, the end in view is attained; if not, the presence of organic substances may be the preventive cause. If, therefore, the flame remains uncolored, shut the pinch-cock at once, and 336

* Zeitschr. f. analyt. Chem., **15**, 505.

† Poggend. Annal., **90**, 600; Chem.-pharm. Centralbl., **1854**, p. 157.

‡ Zeitschr. f. analyt. Chem., **2**. 111.

to the apparatus connect a U-tube containing neutral solution of silver nitrate, open the pinch-cock again, and let the gas pass for many hours, in a slow stream, through the silver solution. If phosphorous acid is present, a precipitate containing silver phosphide will separate in the silver solution; examine it according to 329.*

In this manner, TH. POLECK† has succeeded in detecting phosphorous acid in a body, three months after death, while free phosphorus could no longer be detected.

3. *Examination of the Inorganic Constituents of Plants, Animals, or Parts of the same, of Manures, etc. (Analysis of Ashes).*

§ 265.

A. PREPARATION OF THE ASH.

For the purposes of a qualitative analysis, it is sufficient to incinerate a comparatively small quantity of the substance, which must previously be most carefully cleaned. The incineration is effected best in a small clay muffle, but it may be also conducted in a Hessian crucible placed in a slanting position, or, under certain circumstances, even in a porcelain or platinum dish, with the aid of a wide glass tube or lamp-chimney, to increase the draught. The heat must always be moderate, to prevent the volatilization of certain constituents, especially of chlorides. It is not always necessary to continue the ignition until all the carbon is consumed. With ashes containing a large proportion of fusible salts (as the ash of beet-root molasses), it is best, after thorough carbonization has been effected, to boil with water, and finally to incinerate the washed and dried residue. For further particulars, see my work on quantitative analysis. 337

* W. HERAPATH'S statement (Pharm. Journ., 1865, 573) that phosphoric acid is also reduced by zinc and dilute sulphuric acid is entirely incorrect. (Compare my paper in the Zeitschr. f. analyt. Chem., 6, 208.)

† Zeitschr. f. analyt. Chem., 30, 528.

B. Examination of the Ash.

As the qualitative analysis of an ash is undertaken 338
either as a practical exercise, or for the purpose of determining its general character, and the state in which any given constitutent may happen to be present, or also with a view to make, as far as practicable, an approximate estimation of the quantities of the several constituents, it is usually the best way to examine separately the part soluble in water, the part soluble in hydrochloric acid, and the residue which is insoluble in both. This can be done the more readily, as the number of bodies to be looked for is small.*

a. Examination of the Part soluble in Water.

Boil the ash with water, filter, and while the residue 339
is being washed, examine the solution as follows:

1. To a portion, after heating, add hydrochloric acid in excess, warm, and allow it to stand. Effervescence indicates CARBONIC ACID combined with alkali metals, while the smell of hydrogen sulphide indicates the SULPHIDE of an ALKALI METAL, formed from an alkali-metal sulphate by the reducing action of carbon. Turbidity from separation of sulphur, with smell of sulphur dioxide, denotes a THIOSULPHATE (which occasionally occurs in the ash of coal). Filter if necessary, and add barium chloride to the fluid. A white precipitate indicates SULPHURIC ACID.

2. Evaporate another portion to a small volume, add 340
hydrochloric acid just to acid reaction (effervescence indicates CARBONIC ACID), test a few drops for BORIC ACID, with turmeric-paper (§ 174, 5), evaporate to dryness, and treat

* If the examination should be extended, in exceptional cases, to easily reducible metals which are readily volatile at a red heat (*e. g.*, arsenic, zinc, cadmium and lead), which can be present in plants or animals only under very special circumstances, a treatment is made with hydrochloric acid and potassium chlorate, according to 290 (NOBBE, BÄSSLER, and WILL, Chem. Centralbl., 1884, p. 906).

the residue with hydrochloric acid and water. A residue consists of SILICIC ACID. Filter, evaporate a portion repeatedly almost to dryness with nitric acid, and test with molybdic acid solution, for PHOSPHORIC ACID (§ 172, 10).

3. To another portion add silver nitrate as long as 341
a precipitate continues to form; warm gently, and then cautiously add ammonia. If a black residue is left, this consists of silver sulphide, proceeding from the sulphide of an alkali metal, or from a thiosulphate. Filter, if necessary, then to the ammoniacal liquid add nitric acid in slight excess, to effect the solution of the silver phosphate precipitate formed, thus leaving only SILVER CHLORIDE (iodide, and bromide) undissolved. Filter off the precipitate, and neutralize the filtrate carefully and exactly with ammonia. If this produces a light yellow precipitate, orthophosphoric acid was present, while if the precipitate is white, pyrophosphoric acid was detected in **340**. Test for iodine and bromine, and, if necessary, for chlorine, in a part of the aqueous solution of the ash, according to **178** and **180**.*

4. Heat a portion with hydrochloric acid, then make 342
it alkaline with ammonia, mix it with ammonium oxalate, and allow the liquid to stand. A white precipitate indicates CALCIUM. Filter, and mix the filtrate with ammonia and ammonium sodium phosphate. A crystalline precipitate, which often becomes visible only after long standing, indicates MAGNESIUM. (Magnesium is often found here in distinctly appreciable quantity, but calcium only in exceedingly minute amount, when alkali carbonates and phosphates are present.)

5. Test for POTASSIUM and SODIUM, as directed in **168**, and follow β or α according as magnesium is present or absent.

6. LITHIUM, which is much more frequently found in

* If vegetable or animal matters are to be tested with certainty for the halogens, separate portions must be carbonized with the addition of sodium carbonate, and the aqueous solutions of the residues thus obtained examined. (Compare the corresponding chapter of my "Quantitative Analysis.")

ashes than has hitherto been believed, and RUBIDIUM, which almost constantly accompanies potassium, may be most readily detected by means of the spectroscope, in the residue consisting of the alkali salts (§ 98).

b. Examination of the Part insoluble in Water.

343 1. Warm the greater part of the residue left undissolved by water (after further incineration if it contains much carbon) with hydrochloric acid (effervescence indicates CARBONIC ACID in combination with alkali-earth metals; and evolution of chlorine denotes OXIDES OF MANGANESE). Evaporate to dryness with a few drops of dilute sulphuric acid, heat a little more strongly upon an asbestos support or a sand-bath, to separate the SILICIC ACID, moisten the residue with hydrochloric acid and some nitric acid, add water, warm, and filter from the insoluble residue. Wash this with water, and then test the solution and residue as follows:

a. THE SOLUTION.

344 *aa.* Test a portion with hydrogen sulphide. If this produces any other than a perfectly white precipitate, it must be examined in the usual way. (The ashes of plants occasionally contain COPPER, and if the plant has been manured with excrements deodorized by lead nitrate, they may contain LEAD, and so on).

bb. Mix a portion with ammonia until the resulting precipitate no longer redissolves upon stirring; then add ammonium acetate and some acetic acid, so that the liquid reacts distinctly acid. In most cases, this produces a white precipitate of FERRIC PHOSPHATE, mixed occasionally with some ALUMINIUM PHOSPHATE. Filter, wash the precipitate, heat it with pure potassium hydroxide solution, filter, and test the filtrate for ALUMINIUM by acidifying with hydrochloric acid, adding ammonia, and warming. The

residue insoluble in potassium hydroxide may, if required, be dissolved in hydrochloric acid, and the solution tested with potassium sulphocyanide, for IRON. If the liquid filtered from the precipitate (consisting only or chiefly of ferric phosphate) is reddish, there is more iron present than corresponds to the phosphoric acid; if it is colorless, add ferric chloride drop by drop till the fluid is reddish. (The quantity of the precipitate of ferric phosphate here formed will give some idea of the amount of PHOSPHORIC ACID present.) Heat to boiling the liquid which was reddish, or which has become so by the addition of ferric chloride (if the fluid does not lose its color, add more ammonium acetate and boil again), filter hot, neutralize the filtrate with ammonia (avoiding any considerable excess), and filter again if necessary. Mix the filtrate in a flask (which is to be almost full and closed with a stopper) with yellowish ammonium sulphide, filter off any precipitate that may form after long standing, and test it, according to **139** and beyond, for MANGANESE and ZINC, the latter of which occurs only exceptionally in ashes. Test the liquid in which ammonium sulphide has produced no precipitate, or the liquid filtered from such a precipitate, for CALCIUM (with which some STRONTIUM may be present) and MAGNESIUM, according to §§ 231 and 232.

β. The Residue.

345 The residue insoluble in hydrochloric acid contains the silicic acid which has been separated by treating with hydrochloric acid, and also any barium present, as well as the greater part of any strontium, and possibly some lead, in the form of sulphates, and finally the constituents of the ash, which are, by themselves, insoluble in hydrochloric acid. In most ashes, the latter are sand, clay, and charcoal; substances, therefore, which are present in consequence of defective cleaning or imperfect combustion of the plants, or matter derived from the crucible. It is only the ashes of the stalks of cereals

and other plants abounding in silicic acid that are not completely decomposed by hydrochloric acid. Boil the washed residue for a considerable time with solution of sodium carbonate in excess, filter hot, wash with boiling water, and test for SILICIC ACID in the filtrate, by evaporation with hydrochloric acid, according to § 180, 2. Heat the part of the residue remaining undissolved with very dilute nitric acid, and test this solution by the usual course of analysis, for LEAD, BARIUM, and STRONTIUM.

If the ash was of a kind to be completely decomposed by hydrochloric acid, this part of the analysis may be generally considered as finished, for the accidental admixture of clay and sand will rarely interest the analyst sufficiently to warrant a more minute examination by fusing. But if the ash abounded in silicic acid, and it may therefore be supposed that the hydrochloric acid has failed to effect its complete decomposition, evaporate half of the residue insoluble in solution of sodium carbonate (after extracting it with dilute nitric acid and washing) to dryness, with solution of pure sodium hydroxide in excess, in a silver or platinum dish. This decomposes the silicates of the ash, while affecting the sand but little. Acidify now with hydrochloric acid, evaporate to dryness, and proceed as in 343. For the detection of the alkalies in the part insoluble in water use the other half of the washed residue just mentioned, treating it according to 228. If alkali metals are found here, however, they can be considered as belonging properly to the ash only when the latter was free from clay and other compounds possibly containing alkalies.

2. The remainder of the ash, which has been extracted with water, might be tested for FLOURINE according to § 176, 6; but since flourine is lost in incinerating organic substances containing this element (TAMMANN*), and since, under certain conditions, any flourine not volatilized may go partly into the aqueous extract, it is necessary to examine a separate portion of any animal

* Zeitschr. f. analyt. Chem., 24, 342.

or vegetable substance, in order to insure certainty in regard to flourine. For this purpose, the portion is heated with pure sodium or potassium hydroxide, evaporated to dryness with this, incinerated, and the residue then examined according to § 176, 6.

SECTION III.

EXPLANATORY NOTES AND ADDITIONS TO THE SYSTEMATIC COURSE OF ANALYSIS.

I. Additional Remarks to the Preliminary Examination.

To §§ 211–213.

As already stated, the inspection of the physical properties of a body, especially if it is not a mixture, may enable the analyst in many cases to draw certain general inferences as to its nature. For instance, if the analyst has a white substance before him, he may at once conclude that it is not cinnabar, or if a substance of low specific gravity, that it is not a compound of lead, etc. Inferences of this kind are quite admissible to a certain extent, and are advisable as long as they remain general; but if carried too far, they are apt to mislead the operator by blinding him to every reaction not exactly in accordance with his preconceived notions.

As regards the examination of substances at a high temperature, platinum foil or small iron spoons may also be used in the process; but in most cases, the glass tube gives results more clearly evident, and affords, moreover, the advantage that volatile bodies are less likely to escape detection, and are more readily examined in respect to their nature. To ascertain the products of oxidation of a body, it is sometimes also advisable to heat it in a short glass tube, open at both ends, somewhat contracted at the lower end, and held in a slanting position; small quantities of a metallic sulphide, for instance, may be readily detected by this means (§ 187, 7).

If a substance yields a sublimate (9) when heated in the glass tube, care must be taken about inhaling the vapors which the substance evolves upon heating on charcoal (11), in

order that the injurious vapors of mercury salts or of other poisonous, metallic compounds may not be breathed in large quantities.

With respect to the preliminary examination by means of the blowpipe, it should be mentioned that the student must avoid drawing positive conclusions until he has acquired some practice. A slight coating of the charcoal, which may seem to denote the presence of a certain metal, is not always a conclusive proof of the presence of that metal; nor would it be safe to assume the absence of a substance simply because the blowpipe flame fails to effect reduction, or solution of cobalt nitrate fails to impart a color to the ignited mass, etc. In most cases, the blowpipe reactions are unerring, but it is not always easy to produce them, and they are, moreover, liable to suffer modification by accidental circumstances.

Finally, it may be mentioned, as a matter of experience, that many beginners entirely neglect the preliminary examition in order to save trouble and time, having the idea that they will be able to discover the nature of the substance by means of the actual examination alone. Instead of pointing out the erroneousness of this opinion, it may be mentioned, by way of example, that those who are possessed of this idea are seen searching for hours for the organic acids until they finally find all of them absent. And all this is done to save time and trouble!

II. Additional Remarks to the Solution, etc., of Substances.

To §§ 214–217.

When the characteristics of the classes given in § 214 (into which are divided all substances, with the exception of those which are metallic, according to their behavior with certain solvents) are considered, they seem more sharply defined than is actually the case. This lack of precision is due to the difficultly soluble substances which stand upon the border-line, and it often gives occasion for mistakes on the part of the beginner. Some remarks

concerning this division into classes will, therefore, be made here.

The greatest difficulty occurs in fixing the exact limit between substances which are soluble in water and those that are insoluble in that liquid, since the number of bodies which are sparingly soluble in water is especially large, and the transition from sparingly soluble to insoluble is very gradual. Calcium sulphate, which is soluble in about 450 parts of water, might perhaps serve as a limit between the two classes, since this salt may be positively detected in its aqueous solution by the delicate reagents for calcium and sulphuric acid.

When examining an aqueous fluid by evaporating a few drops of it upon platinum foil, to see whether it holds a solid body in solution, a very minute residue sometimes remains, which leaves the analyst in doubt respecting the conclusion to be drawn. In cases of this kind, in the first place, test the reaction of the fluid with litmus-papers; in the second place, add to a portion a drop of solution of barium chloride; and lastly, to another portion, add some dissolved sodium carbonate. Should the fluid be neutral, and remain unaltered upon the addition of these reagents, the analyst need not, as a general rule, examine it further for metals or acids; for if the fluid contained any of those metals or acids which principally form sparingly soluble compounds, the reagents employed would have revealed their presence. The analyst may therefore feel assured that the detection of the substance of which the residue left upon evaporation consists will be more readily effected in the class of bodies insoluble in water.

If water has dissolved any part of the substance under examination the student will always do well to examine the solution by itself both for acids and bases, since this will lead more readily to a correct apprehension of the nature of the compound and will give greater certainty—two advantages which will amply counterbalance the drawback of sometimes meeting with the same substance both in the aqueous and in the acid solution.

The following substances (with few exceptions) are insoluble in water, but soluble in hydrochloric or nitric acid: The

phosphates, arsenates, arsenites, borates, carbonates, and oxalates of all but the alkali metals; also various tartrates, citrates, malates, benzoates, salicylates, and succinates; the oxides, hydroxides, and sulphides of the heavy metals; alumina, magnesia; many of the metallic iodides and cyanides, etc. Nearly all these bodies are decomposed by boiling concentrated hydrochloric acid, if not by the dilute acid (see § 239 for the exceptions), but this decomposition gives rise to the formation of insoluble or sparingly soluble compounds in the presence of silver, mercury (in mercurous salts), and lead. This is not the case with nitric acid, and accordingly the latter effects complete solution in many cases where hydrochloric acid leaves a residue. On the other hand, however, besides the bodies insoluble in any simple acid, nitric acid leaves antimonious oxide, stannic acid, manganese dioxide, lead dioxide, etc., undissolved, and dissolves many other substances less readily than hydrochloric acid (*e.g.*, ferric oxide and alumina).

Substances not soluble in water are therefore to be treated as follows: Try to dissolve them in dilute or concentrated, cold or boiling, hydrochloric acid; if this fails to effect complete solution, try to dissolve a fresh portion in nitric acid; and if this also fails, treat the body with aqua regia, which is an excellent solvent, more particularly for metallic sulphides. To examine separately the solution in hydrochloric or in nitric acid, on the one hand, and that in nitro-hydrochloric acid on the other, is, in most cases, neither necessary nor desirable. To prepare a solution in nitric acid, or in aqua regia, where the nature of the substance does not demand it, is not advisable, as a solution in hydrochloric acid is much better suited for precipitation by hydrogen sulphide. Nor is it advisable to concentrate a solution in aqua regia by evaporation, in order to drive off the excess of the acids, as the operation might lead to the partial escape, at least, of volatile chlorides—mercuric chloride, for example. It is therefore always best to use no more aqua regia than is necessary to effect solution. Solutions prepared with hydrochloric acid generally contain the metals in the same state of oxidation in which they were originally present (the peroxides and oxides resembling these, form exceptions, and also mercurous com-

pounds, since mercurous chloride when boiled with hydrochloric acid for a long time gradually decomposes into the metal and mercuric chloride). On the other hand, solutions prepared with nitric acid or aqua regia frequently contain the metals in a higher state of oxidation. Thus, ferrous, stannous, and arsenious compounds are converted into ferric, stannic, and arsenic compounds, a circumstance which should always be borne in mind.

With regard to the solution of metals and alloys, it should be mentioned that, upon boiling them with nitric acid, white precipitates will frequently form, although neither tin, antimony, nor silicon (44) are present. Inexperienced students often confound such precipitates with the oxides of these elements, although their appearance is quite different. These precipitates consist simply of nitrates sparingly soluble in the nitric acid present, but readily soluble in water. Consequently the analyst should ascertain whether these white precipitates will dissolve in water before he concludes that they consist of tin or antimony, etc.

III. Additional Remarks to the Actual Analysis.

To §§ 218–240.

A. General Review and Explanation of the Analytical Course.

a. Detection of the metals.

In Part I, Section III, which treats of the behavior of bodies with reagents, the metals have been divided into six groups, and in the section just mentioned it has been shown how the metals of each group are separated from each other or are recognized in the presence of each other. In general, these groups are the same as those into which we separate the metals in the course of analysis. The course of analysis set forth in §§ 225–234, in which the presence of all the metals taken into consideration is assumed, is based upon this separation into groups, and upon the recognition of the individual metals of these groups. In the course

just mentioned, it was of primary importance to give a practical introduction to the process of actual analysis. On account of this aim, much had to be inserted which is not necessary for a purely theoretical comprehension of the subject, and which is rather an impediment to a rapid summary of it. Since such a comprehension and summary appear to be the most indispensable requirements for successful work, the key to the process, as far as the separation of the groups is concerned will be briefly given here. Regarding the detection of the metals individually, reference is made to to what is said under the heading "Recapitulation and Remarks," from § 93 to § 157.

The general reagents which serve to divide the metals into principal groups are—HYDROCHLORIC ACID, HYDROGEN SULPHIDE, AMMONIUM SULPHIDE, and AMMONIUM CARBONATE; and this is likewise the order of succession in which they are applied. Ammonium sulphide performs a double part, in one of which it is sometimes replaced by sodium sulphide.

Let us suppose we have simultaneously in solution all the metals considered in the course of analysis, including both arsenious and arsenic acids, and also calcium phosphate, the latter serving as a type of the salts of the alkali-earth metals, soluble in acids, and reprecipitated unaltered by ammonia.

Chlorine forms insoluble compounds only with silver and mercury (in the mercurous state); while lead chloride is sparingly soluble in water. If, therefore, we add to our solution

1. *Hydrochloric Acid,*

we remove from it the metals of the first division of the fifth group, viz., the whole of the SILVER and the whole of the MERCURY existing in MERCUROUS form. From concentrated solutions, a portion of the LEAD may likewise precipitate as chloride, but this is immaterial, as a sufficient quantity of the lead remains in the solution to permit the subsequent detection of this metal.

Hydrogen sulphide completely precipitates the metals of the fifth and sixth groups from solutions containing a free mineral acid. But none of the other metals are precipitated under these circumstances, since those of the first and second

groups (not considering the fact that their sulphides cannot exist in acid solutions) form no sulphur compounds which are insoluble in water; the sulphides of the third group (aluminium sulphide and chromium sulphide) cannot be formed in the wet way; while those of the fourth group, although they are insoluble in water, cannot exist in presence of mineral acids in excess.

If, therefore, after the removal of silver and (mercurous) mercury, by means of hydrochloric acid, we add to the solution, which still contains free hydrochloric acid,

2. *Hydrogen Sulphide*,

we remove from it the remainder of the metals of the fifth, together with those of the sixth group, viz., LEAD, (mercuric) MERCURY, COPPER, BISMUTH, CADMIUM, as well as GOLD, PLATINUM, TIN, ANTIMONY, and ARSENIC. All other metals remain in solution, either unchanged in their state of oxidation or reduced to a lower one (*e. g.*, ferric compounds and chromic acid).

The sulphides (at least the higher sulphides) of the metals of the sixth group combine with the sulphides of the alkali metals or ammonium, and form sulphur salts soluble in water; but the sulphides of the metals of the fifth group do not possess this property, or possess it only to a limited extent. (Mercuric sulphide dissolves in sodium sulphide and in potassium sulphide, but it is as good as insoluble in ammonium sulphide; while copper sulphide dissolves slightly in ammonium sulphide, but not in potassium or sodium sulphide.) If, therefore, we treat the whole of the sulphides precipitated by hydrogen sulphide from an acid solution, with

3. *Ammonium Sulphide* (or if the case requires it, *Sodium Sulphide*),

with the addition, if necessary, of some sulphur or yellow ammonium sulphide, the sulphides of mercury, lead, copper, bismuth, and cadmium, remain undissolved, while the other sulphides dissolve completely as compounds of the sulphides of GOLD, PLATINUM, ANTIMONY, TIN, ARSENIC, with ammonium sulphide (or sodium sulphide), and precipitate again from this solution upon the addition of hydrochloric acid, either unaltered or in a state of higher sulphuration (they take up

sulphur from the yellow ammonium sulphide). The acid decomposes the sulphur salt formed. The sulphur base (ammonium sulphide or sodium sulphide) is decomposed by hydrochloric acid into the chloride and hydrogen sulphide, and the liberated sulphur acid precipitates. Sulphur precipitates at the same time, if the ammonium sulphide contains an excess of that element. The analyst must bear in mind that this separated sulphur makes the precipitated sulphides appear of a lighter color than they are naturally.

The sulphides corresponding to the metals still remaining in solution are part of them (as those of the alkali and alkali-earth metals) soluble in water; part (as those of aluminium and chromium) cannot form in the wet way; and part (as those of the fourth group) are insoluble in water. The last would, accordingly, have been precipitated by hydrogen sulphide, but for the free acid present. If, therefore, this free acid is removed, *i.e.*, if the solution is made alkaline, and then treated with more hydrogen sulphide, if required, or, what will answer both purposes at once, if

4. *Ammonium Sulphide*

is added to the solution (after previous neutralization of the free acid by ammonia, to prevent unnecessary evolution of hydrogen sulphide, and after previous addition also, if necessary, of ammonium chloride, to prevent the precipitation of magnesium hydroxide by ammonia), the sulphides of the metals of the fourth group will precipitate, viz., the SULPHIDES of IRON, MANGANESE, COBALT, NICKEL, and ZINC. But in conjunction with them, ALUMINIUM HYDROXIDE, CHROMIC HYDROXIDE, and CALCIUM PHOSPHATE are thrown down, because the acids of the aluminium and chromic salts, and the acid which has kept the calcium phosphate in solution, have gone over into ammonium salts, in which the separated hydroxides as well as the calcium phosphate are insoluble.

There remain now in solution only the alkali-earth metals and the alkali metals. The normal carbonates of the former are as good as insoluble in water, while those of the latter are soluble. If, therefore, we now add

5. *Ammonium Carbonate,*

together with a little free ammonia, to guard against the pos-

sible formation of bicarbonates, the whole of the alkali-earth metals might be expected to precipitate. This is, however, the case only as regards BARIUM, STRONTIUM, and CALCIUM.* Of magnesium, we know that, owing to its disposition to form soluble compounds with ammonium salts, it precipitates only in part; and that the presence of additional ammonium salt will altogether prevent its precipitation, at least within a short time. To guard against any uncertainty arising from this cause, ammonium chloride, if it is not already present in sufficient amount, is added previously to the addition of the ammonium carbonate, and after the latter has acted for a short time the liquid is filtered, and thus the precipitation of the magnesium is altogether prevented.

We have now still in solution MAGNESIUM and the ALKALI METALS. The detection of magnesium may be effected by means of ammonium sodium phosphate and ammonia; but its separation requires a different method, since the presence of sodium and phosphoric acid would impede the further progress of the analysis. The process which serves to effect the removal of the magnesium is based upon the insolubility of magnesium hydroxide. The residue obtained by evaporating the solution to dryness is accordingly ignited in order to expel the ammonium salts, any sulphuric acid or other acid present forming a barium salt insoluble in water, which would impede the detection of the alkali metals, is removed by the addition of barium chloride, and the magnesium is precipitated as hydroxide by means of barium hydroxide or milk of lime, whereupon the alkali metals remain in solution together with soluble barium (and calcium) compounds. By the addition of ammonium carbonate, the barium and calcium compounds are removed from the solution, which now only contains the alkali metals and the ammonium salts that have been formed and have been added in excess. If the

* It has been already explained in § 104 that traces of these remain in solution, partly because their carbonates are not absolutely insoluble in water, but principally because they are noticeably soluble in ammonium chloride solution. On account of this deportment, the filtrate from the ammonium carbonate precipitate is tested with ammonium sulphate and oxalate in 169. In the general explanation of the course given in the text, these traces of barium, strontium, and calcium, are not taken into account.

ammonium salts are then removed by ignition, the residue consists of the alkali-metal chlorides alone. But as barium carbonate and calcium carbonate are slightly soluble in ammonium salts, and give barium chloride and calcium chloride upon evaporation with ammonium chloride, it is usually necessary, after the expulsion of the ammonium salts by ignition, to precipitate once more with a little ammonium carbonate and a drop or two of ammonia, in order to obtain a solution perfectly free from barium and calcium, in which POTASSIUM and SODIUM may now be detected without difficulty.

Lastly, to effect the detection of the AMMONIUM, a fresh portion of the substance must, of course, be taken.

b. Detection of the acids.

Before passing on to the examination for acids and halogens, the analyst should ask himself which of these can be present, judging from the class to which the substance under examination belongs with respect to its solubility, since this will save making unnecessary experiments. Upon this point, the beginner will find the table in Appendix IV useful.

For the detection of the acids, the general reagents applied, as we have seen, are BARIUM CHLORIDE and SILVER NITRATE for the inorganic acids, and for the organic acids, CALCIUM CHLORIDE and FERRIC CHLORIDE. It is therefore indispensable that the analyst should first assure himself whether the substance under examination contains only inorganic acids, or whether organic acids must also be looked for. The latter is invariably the case if the body, when ignited, turns black, owing to separation of carbon. In the examination for metals, the general reagents serve to effect the actual separation of the several groups of metals from each other; but in the examination for acids, they serve chiefly to demonstrate the presence or absence of the acids belonging to the different groups.

Let us suppose that we have an aqueous solution containing all the acids, in combination with sodium, for instance.

Barium forms insoluble, or difficultly soluble, compounds with sulphuric, phosphoric, arsenious, arsenic, carbonic,

silicic, boric, chromic, oxalic, tartaric, and citric acids; barium fluoride is also insoluble, or at least only sparingly soluble; and all these compounds are soluble in hydrochloric acid, with the exception of barium sulphate. If, therefore, to a portion of the neutral, or, if necessary, neutralized solution, we add

1. *Barium Chloride,*

the formation of a precipitate denotes at once the presence of at least one of these acids. By treating the precipitate with hydrochloric acid, we learn that sulphuric acid is present, as all the other barium salts dissolve, while barium sulphate remains undissolved. Where barium sulphate is present, the reaction with barium chloride shows positively the presence of only a part of the other acids enumerated; for upon filtering the hydrochloric acid solution of the precipitates, and supersaturating the filtrate with ammonia, the borate, tartrate, citrate, etc., of barium do not always fall down again, being kept in solution by the ammonium choride formed. For this reason, barium chloride cannot serve to effect the actual separation of all the acids named, and, except as regards sulphuric acid, no value is placed upon this reagent as a means of effecting their individual detection. Still it is of great importance as a reagent, because the non-formation of a precipitate upon its application in neutral solutions proves at once the absence of so considerable a number of acids.

The compounds of silver with sulphur, chlorine, iodine, bromine, cyanogen, ferrocyanogen, ferricyanogen, and sulphocyanogen, and with phosphoric, arsenious, arsenic, boric, chromic, silicic, oxalic, tartaric, and citric acids, are insoluble, or difficultly soluble in water. All these compounds are soluble in dilute nitric acid, with the exception of the chloride, iodide, bromide, cyanide, ferrocyanide, ferricyanide, sulphocyanide, and sulphide of silver. If, therefore, we add to our solution, which, for the reason just stated, must be perfectly neutral,

2. *Silver Nitrate,*

and precipitation ensues, this shows at once the presence of one or several of the acids enumerated, but, as far as the most

of them are concerned, only in a general way. Chromic acid, arsenic acid, and several others, which form colored salts with silver, may be individually recognized with tolerable certainty by the mere color of the precipitate. By now treating the precipitate with nitric acid, we see whether it contains silver sulphide or any of the halogen compounds of silver, as these remain undissolved, while all the oxygen salts dissolve. Silver nitrate fails to effect the complete separation of those acids which form with silver compounds insoluble in water, from the same cause which renders the separation of acids by barium chloride uncertain, viz., the ammonium salt formed prevents the reprecipitation by ammonia of several of the silver salts from the acid solution. Silver nitrate, besides effecting the separation of chlorine, bromine, iodine, cyanogen, etc., and indicating the presence of chromic acid, etc., serves, like barium chloride, to demonstrate at once the absence of a great many acids, where it produces no precipitate in neutral solutions.

The deportment which the solution under examination exhibits with barium chloride and with silver nitrate, at once indicates, therefore, the further course of the investigation. For instance, where barium chloride has produced a precipitate, while silver nitrate has failed to do so, it is not necessary to test for phosphoric, chromic, boric, silicic, arsenious, arsenic, oxalic, tartaric, and citric acids, provided always that the solution was sufficiently concentrated and did not already contain ammonium salts. A similar conclusion may be drawn if a precipitate is obtained by silver nitrate, but none by barium chloride. It is obvious that many separate experiments may be saved by these simple combinations.

Returning now to the supposition which has been made here, viz., that all the acids are present in the solution under examination, the reactions with barium chloride and silver nitrate would accordingly have already demonstrated the presence of SULPHURIC ACID and led to the application of the special tests for CHLORINE, BROMINE, IODINE, CYANOGEN, FERROCYANOGEN, FERRICYANOGEN, SULPHOCYANOGEN, and SULPHUR (the separation and special detection of which is explained in § 188), and there would be reason to test for all the other acids precipitable by either of these two reagents. The detection

of these acids is based entirely upon the results of special experiments, which have already been fully described and explained in the course of the present work, and may be passed over here. The same remark applies to the rest of the inorganic acids, that is, to nitric acid and chloric acid.

Of the ORGANIC ACIDS, oxalic, racemic, and tartaric acids are precipitated by calcium chloride in the cold, in presence of ammonium chloride; the two former immediately, the latter often only after some time; but the precipitation of calcium citrate is prevented by the presence of ammonium salts, and ensues only upon ebullition or upon mixing the solution with alcohol. The latter agent also serves to effect the separation of calcium malate and succinate from aqueous solutions containing ammonium chloride. If, therefore, we add to our fluid

3. *Calcium Chloride in excess and Ammonium Chloride,*

OXALIC ACID, RACEMIC ACID, and TARTARIC ACID are precipitated, but the calcium salts of several inorganic acids (calcium phosphate, for instance), if such are present, precipitate along with them. We must therefore select for the individual detection of the precipitated organic acids, only such reactions as preclude the possibility of confounding the organic acids with the inorganic acids that are thrown down along with them. For the detection of oxalic acid, we select, accordingly, solution of calcium sulphate, with acetic acid (§ 175, 5); to effect the detection of the tartaric and racemic acids, we treat the precipitate produced by calcium chloride with solution of caustic soda, since the calcium salts of these two acids only are soluble in this solution in the cold, but insoluble upon boiling.

Of the organic acids, we have now still in solution citric and malic acids, succinic, salicylic, and benzoic acids, acetic and formic acids. CITRIC ACID, MALIC ACID, and also SUCCINIC ACID precipitate upon addition of alcohol to the fluid filtered from the oxalate, tartrate, etc., of calcium, if it still contains an excess of calcium chloride. Sulphate and borate of calcium invariably precipitate along with the malate, citrate, and succinate of calcium, if sulphuric acid and boric acid happen to be present. The analyst must therefore carefully guard against confounding the calcium precipitates of these

acids with those of citric acid, malic acid, and succinic acid. The alcohol is now removed by evaporation, and

4. *Ferric Chloride*

added to the neutral fluid. This reagent precipitates the BENZOIC ACID as a ferric salt, while SALICYLIC ACID (which is to be recognized by the violet coloration of the liquid), FORMIC ACID, and ACETIC ACID remain in solution. The methods which serve to effect the further separation of the groups, and the reactions on which the individual detection of the various acids is based, have been fully described and explained in the former part of this work, and cannot, therefore, be repeated here.

B. Special Remarks and Additions to the Systematic Course of Analysis.

Attention will be called here to several matters which were necessarily passed over in the description of the ordinary course of analysis, and the present opportunity is taken to explain, in finer print, how the course may be expanded to meet the detection of RARE METALS.

To § 225.

At the commencement of § 225, the analyst is directed to mix NEUTRAL or ACID aqueous solutions with hydrochloric acid. This should be done drop by drop. If no precipitate forms, a few drops are generally sufficient, since in that case, the only object is to acidify the fluid in order to prevent the subsequent precipitation of the metals of the iron group by hydrogen sulphide. In the case of the formation of a precipitate, some chemists recommend that a fresh portion of the solution should be acidified with nitric acid. However, even leaving the fact out of consideration, that nitric acid also produces precipitates in many cases (in a solution of potassium antimonious tartrate, for instance) the use of hydrochloric acid, *i.e.*, the complete precipitation by that acid of all that is precipitable by it, is to be preferred for the following reasons: 1. Metals are more readily precipitated by hydrogen sulphide from solutions

acidified with hydrochloric acid than from those acidified with nitric acid; 2. In cases where the solution contains silver, (mercurous) mercury, or lead, the further analysis is materially facilitated by the total or partial precipitation of these metals in the form of chlorides; and 3. The latter form is the best adapted for the individual detection of these three metals when present in the same solution, and, further, the application of hydrochloric acid saves the necessity of examining to find whether the mercury, which may be subsequently detected with the other metals of the fifth group, was originally present in the mercurous or mercuric form. That the lead, if present in large proportion, is obtained partly in the form of a chloride, and partly in the precipitate produced by hydrogen sulphide in the acid solution, can hardly be urged as an objection to the application of this method, for the removal of the larger portion of the lead from the solution, effected at the commencement, will only serve to facilitate the examination for other metals of the fifth and sixth groups.

As already stated, along with the two insoluble chlorides and the difficultly soluble lead chloride, a basic antimonious salt may separate (*e. g.*, from tartar emetic or an analogous compound), also basic bismuth chloride and metastannic chloride, and finally also silicic acid, benzoic acid, and salicylic acid. But since basic antimonious salts as well as basic bismuth chloride are soluble in an excess of hydrochloric acid, these go into solution when the amount of hydrochloric acid is increased. They have no influence, therefore, upon the rest of the process. The application of heat to the fluid mixed with hydrochloric acid is neither necessary nor even advisable, since it might cause the conversion of a little of the precipitated mercurous chloride into mercuric chloride.

Should bismuth, antimony, lead, or metastannic acid be present, the addition to the first filtrate of the water used for washing the precipitate produced by hydrochloric acid may cause turbidity or a precipitate. In the case of bismuth and antimony, this is occasioned by an insufficiency of free hydrochloric acid to prevent the separation of basic salts; but in the case of lead chloride and metastannic acid, by the lead chloride or metastannic chloride dissolving in the wash-water, and then meeting with sufficient hydrochloric

acid in the filtrate for reprecipitation. The subsequent process, however, is not modified on account of this turbidity or precipitation, since hydrogen sulphide as readily converts these finely divided precipitates into sulphides as if the metals were in actual solution.

If benzoic acid or salicylic acid should be mixed with the precipitate treated with an excess of hydrochloric acid, and washed with cold water, these would then dissolve with the lead chloride in the subsequent treatment with hot water, but they would not interfere with the detection of lead in this solution.

In the case of ALKALINE solutions, the addition of hydrochloric acid must be continued until the fluid shows a strongly acid reaction. The substance which causes the alkaline reaction combines with the hydrochloric acid, and the bodies originally dissolved in that alkaline substance separate. Thus, if the alkali was combined with metallic oxides, zinc hydroxide, alumina, etc., may precipitate here. But these hydroxides will redissolve in an excess of hydrochloric acid, whereas silver chloride or silicic acid will not redissolve, and lead chloride only with difficulty. If a metallic sulphur salt is the cause of the alkaline reaction, the sulphur acid (*e.g.*, antimonic sulphide) precipitates upon the addition of the hydrochloric acid, while the sulphur base (*e.g.*, sodium sulphide) forms with the constituents of the hydrochloric acid, sodium chloride, and hydrogen sulphide. If a carbonate, a cyanide, or a sulphide of an alkali metal is the cause of the alkaline reaction, carbonic acid, hydrocyanic acid, or hydrogen sulphide escapes. All these phenomena should be carefully observed by the analyst, since they not only indicate the presence of certain substances, but demonstrate also the absence of entire groups of bodies.

Precipitates are also produced by hydrochloric acid in solutions containing thallious salts, alkali-metal salts of antimonic, tantalic, niobic, molybdic, and tungstic acids.* The precipitates originating from antimonic, tantalic, and molybdic acids dissolve (the tantalic acid to an opalescent fluid), while THALLIOUS CHLORIDE, NIOBIC ACID, and TUNGSTIC ACID do not dissolve, or

* From solutions of metatungstates, hydrochloric acid precipitates common tungstic acid, but only after long-continued boiling.

are but slightly soluble, in an excess of hydrochloric acid. The latter, therefore, remain with the precipitate, which may also contain silver chloride, mercurous chloride, lead chloride, and silicic acid. Separation of sulphur ensuing after some time on addition of hydrochloric acid, accompanied by the odor of sulphurous acid, indicates THIOSULPHURIC ACID. If it is desired to test for rare metals, after exhausting the precipitate with boiling water, examine the fluid for THALLIUM by potassium iodide (confirming by the spectroscope). On exhausting with water and treating with ammonia, the silver chloride is wholly or at least partly dissolved, and also any tungstic acid present. From this solution, ammonium sulphide then precipitates silver sulphide, and from the filtrate from this, dilute hydrochloric acid precipitates tungstic sulphide. By the treatment with ammonia, mercurous chloride is converted into a black mixture of very finely divided mercury and the so-called infusible white precipitate, with which silver chloride may remain (J. BARNES, MOECK). (Compare § 138.) If the residue is treated as is there directed, the metallic silver may be extracted with dilute nitric acid, the silicic acid may be volatilized with hydrofluoric and sulphuric acids, and the niobic acid remaining behind may be dissolved in aqueous hydrofluoric acid, after fusion with potassium disulphate.

To §§ 226 and 227.

A judicious distribution and economy of time are especially to be studied in the practice of analysis; and many of the operations, which the student may readily perceive and arrange for himself, may be carried on simultaneously. For instance, after making a precipitation with hydrogen sulphide, instead of folding one's hands until the precipitate is fully washed, the first drops of the filtrate may be tested with ammonium sulphide to see if there is any metal of that group present, and if this is not the case, the operator may proceed to test with ammonium carbonate. He will thus be able, while washing the hydrogen sulphide precipitate, to treat the filtrate with the proper group reagent. Again, while digesting the first precipitate with ammonium sulphide, the second precipitate may be washed, etc. When the student has accustomed himself to distribute his time in this way, he can accomplish more in one hour, without working at all hastily, than he otherwise would do in two.

In cases where the analyst has simply to deal with metals of the sixth group (*e.g.*, antimony) and of the fourth or fifth group (*e.g.*, iron or bismuth), he need not precipitate the acid-

ified solution with hydrogen sulphide, but may, after neutralization, at once add ammonium sulphide in excess. The iron, etc., will in that case precipitate, while the antimony, etc., will remain in solution, from which, by addition of an acid, they will be thrown down at once as antimonious sulphide, etc. This method has the advantage that the fluid is diluted less than in the case where solution of hydrogen sulphide is employed, and that the operation is performed more expeditiously and conveniently than is the case where hydrogen sulphide gas is conducted into the fluid. Attention must again be called to the very constant occurrence of mistakes through the use of spoiled or too weak hydrogen sulphide water, through the use of an insufficient quantity of hydrogen sulphide water, or through passing the gas into a solution containing a TOO LARGE EXCESS of hydrochloric or nitric acid. Imagine a very acid solution containing iron and bismuth. If hydrogen sulphide gas is passed into it, or a few drops of the water are added, no precipitate will be produced, for the presence of the great excess of concentrated hydrochloric acid makes its formation impossible. If, with the idea that no metal of the hydrogen sulphide group is present, ammonium sulphide is then added, a precipitate containing the sulphides of iron and bismuth will be obtained, and on treating this with dilute hydrochloric acid, the bismuth sulphide will remain as a black residue, indicating the presence of nickel or cobalt. As soon as the right path has once been left in this manner, it is extremely difficult, or even almost impossible, for the beginner to find the way again. There is scarcely another rock in the whole course of analysis upon which analyses are more frequently wrecked, especially where gaseous hydrogen sulphide is used, and where the fact is so frequently unheeded that the precipitate cannot form in very acid solutions unless they are diluted with water. Arsenic acid also may be very easily overlooked unless the action of hydrogen sulphide is facilitated by the application of a proper degree of heat for a sufficient length of time. The indicated difficulties may be avoided if a portion of the liquid filtered from the hydrogen sulphide precipitate is taken, before its treatment with ammonium sulphide is proceeded with, and about four volumes of good hydrogen sulphide water are added to it, and it is ob-

served whether a further precipitation is thus produced, either in the cold or upon warming.

While the treatment of a too concentrated solution, containing too much hydrochloric acid, with hydrogen sulphide, especially with the gas, interferes with the proper performance of the analysis, it is also possible, on the other hand, for difficulties to arise from the addition of too small an amount of hydrochloric acid, because in that case, especially in the presence of certain salts (*e.g.*, alkali-metal acetates), sulphides of the fourth group, also, especially zinc sulphide, may go into the precipitate containing the sulphides of the fifth and sixth groups. Sometimes this cannot be prevented, even by an increased addition of hydrochloric acid, and, therefore, in the examination of the sulphides of the fifth group in the course of analysis, it must be taken into consideration, that metals of the fourth group, especially zinc, may possibly be found here also.

In like manner, the insufficient washing of the precipitate obtained by hydrogen sulphide from a solution acidified with hydrochloric acid often gives rise to mistakes, and to an entirely unnecessary retardation of the analysis. Mistakes may occur, because mercuric sulphide is insoluble in hot nitric acid, only when it contains no hydrochloric acid, and unnecessary intricacies result when the improperly washed precipitate is tested with ammonium sulphide to find whether it is wholly soluble, not at all soluble, or partly soluble, in this reagent. It is evident that this important decision cannot be made if a solution containing iron, nickel, etc., still adheres to the precipitate.

In treating acid solutions with hydrogen sulphide, or in decomposing by hydrochloric acid the ammonium sulphide used to effect the solution of sulphides of the sixth group, it occasionally happens that precipitates are obtained which look almost like pure sulphur, and thus leave the analyst in doubt as to whether it is really requisite to examine them for metals. In such cases, however, a decision may be reached with certainty by shaking with benzol or petroleum-ether, as prescribed in the course of analysis, since these solvents effect the solution of the finely divided sulphur, but not that of the metallic sulphides. It is there-

fore unnecessary to follow the formerly customary, more roundabout way of treating the washed precipitate with a solution of bromine in hydrochloric acid, or with hydrochloric acid and some potassium chlorate, diluting, filtering, and, after driving off the free bromine or chlorine by heating, treating the liquid anew with hydrogen sulphide in order to detect the presence of metals of the fifth or sixth groups. If it should be preferred to use the precipitate, freed from sulphur by means of benzol or petroleum-ether, directly for further examination, pour the liquid containing it upon a moistened filter, allow the aqueous liquid to run off, and then pour absolute alcohol upon the filter. After the alcoholic liquid has passed through the filter, wash the precipitate, first with alcohol, then with water, and use it for further examination.

The following sulphides of the rarer elements pass into the precipitate produced by hydrogen sulphide in an acid solution : The sulphides of palladium, rhodium, osmium, ruthenium, iridium,* germanium, molybdenum, tellurium, selenium, and possibly of thallium.†

The following rare compounds cause separation of sulphur, by decomposing the hydrogen sulphide : The higher oxides and chlorides of manganese and cobalt, vanadic acid (with blue coloration of the fluid), nitrous acid, sulphurous acid, and thiosulphuric acid, hypochlorous and chlorous acids, bromic acid, and iodic acid.

On treating the precipitate with ammonium sulphide (or sodium sulphide), the sulphides of germanium, iridium, molybdenum, tellurium, and selenium, dissolve (with the sulphides of arsenic, antimony, etc.), while the sulphides of palladium, rhodium, osmium, and ruthenium, and of the thallium possibly present here, remain undissolved (with the sulphides of lead, bismuth, etc.).

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* The metals of the platinum ores are precipitated with difficulty by hydrogen sulphide. To attain the end in view, hydrogen sulphide gas must be perseveringly conducted into the fluid, and heat applied at the same time. In regard to their separation, compare MYLIUS and FÖRSTER, Ber. d. deutsch. Chem. Gesellsch., 1892, p. 665.

† Tungsten and vanadium are not found in the precipitate thrown down from an acid solution by hydrogen sulphide. They can be present only where the fluid has been first mixed with ammonium sulphide, then with acid in excess ; but in that case, the sulphides of nickel and cobalt will also be found with those of the fifth and sixth groups. Thallium, although it is not precipitated from acid solutions by hydrogen sulphide under ordinary circumstances, may be thrown down in combination with the sulphides of arsenic or antimony.

To § 228.

Two methods for separating the metallic sulphides of the sixth group are described in § 228, one of which is to be used when there is cause to leave the presence of gold and platinum out of consideration, while their presence is taken into consideration in the other. The latter, in which the sulphides are heated in the first place with a mixture of ammonium chloride and nitrate, is also to be used when IRIDIUM may be present. This metal remains behind with gold and platinum, while all the other elements are present in the resulting sublimate, and may be precipitated again from its solution, by means of hydrogen sulphide.

If the sulphides, thus obtained, of the remaining elements of the sixth group—that is, those of tin, antimony, arsenic, germanium, tellurium, selenium, and molybdenum—are fused with sodium carbonate and nitrate, as described in § 228, and the mass is treated with cold water, GERMANIC OXIDE, TELLURIC ACID, SELENIC ACID, and MOLYBDIC ACID go into solution with the arsenic acid, while stannic oxide and sodium antimonate remain behind.

The manner in which the rarer elements in the solution and the iridium in the residue from the sublimation may be detected, follows from §§ 158–163.

To § 229.

The separation of the sulphides of the fifth group from those of the sixth by ammonium or sodium sulphide is not always complete, especially with only one treatment. Under certain conditions, it is therefore possible for portions of the sulphides of Group VI to be present with the sulphides of the fifth group, and this is especially the case with the sulphides of gold and platinum, on which account these sulphides must be taken into consideration also in § 229. Since the solution of platinic nitrate (which is obtained if the platinic sulphide was precipitated in the cold) is brown, the presence of platinum with the metals of Group V is sometimes recognized simply by the brown color shown by the solution which is obtained by heating the sulphides with nitric acid. If such a brown solution is evaporated to dryness, ignited, and the residue is heated with nitric acid, the platinum remains behind in the metallic state, while the oxides of the other metals dissolve.

Besides the methods described in the systematic course, to

separate cadmium, copper, lead, and bismuth, the following process will also be found to give highly satisfactory results: Add sodium carbonate to the nitric acid solution as long as a precipitate continues to form, then solution of potassium cyanide in excess, and heat gently. This effects the complete precipitation of lead and bismuth in the form of carbonates, while copper and cadmium are obtained in solution in the form of potassium copper cyanide and potassium cadmium cyanide. Lead and bismuth may now be readily separated from each other by means of sulphuric acid. The separation of the copper from the cadmium is effected by adding to the solution of the cyanides of these two metals in potassium cyanide, hydrogen sulphide in excess, gently heating, and then adding some more potassium cyanide, in order to redissolve the copper sulphide which may have precipitated along with the cadmium sulphide. A residuary yellow precipitate (cadmium sulphide), insoluble in the potassium cyanide, demonstrates the presence of cadmium. Filter the fluid from this precipitate, and add hydrochloric acid to the filtrate, when the formation of a black precipitate (cupric sulphide) will demonstrate the presence of copper. Since hydrocyanic acid is set free by the addition of hydrochloric acid, the operation must be performed under a hood.

Where there is reason to suppose that the precipitate of the sulphides of the fifth group contains the sulphides of palladium, rhodium, osmium, ruthenium, or thallium, with cupric sulphide, bismuth sulphide, etc., first test a portion in the spectroscope for thallium, and then proceed as follows with the main part of the precipitate:

Fuse the precipitate with potassium hydroxide and chlorate, heat ultimately to redness, let the mass cool, then treat it with water. Besides the compound of lead oxide with potassium hydroxide, the solution contains potassium perosmate and ruthenate, the latter imparting a deep yellow color to it. By passing in carbon dioxide, the lead may be precipitated. If the filtrate is cautiously neutralized with nitric acid, black, hydrated RUTHENIUM SESQUIOXIDE separates; while if more nitric acid is added to the filtrate, and the fluid then distilled, PEROSMIC ACID passes over. If the residue left upon the extraction of the fused mass with water is gently ignited in hydrogen gas (any cadmium present might escape in this operation), then cautiously treated with dilute nitric acid, the copper, lead, etc., are dissolved, while the rhodium and palladium are left undissolved. The PALLADIUM may then be dissolved out of the residue by means of aqua regia, leaving the RHODIUM undissolved. For the further examination of

the separated metals, refer to §§ 144–147. In the event of the foregoing process being adopted, a separate portion of the precipitate of the sulphides must be examined for mercury.

To § 230.

Assuming all elements not yet precipitated to be present in the fluid filtered from the precipitate produced in an acid solution by hydrogen sulphide, the precipitate produced in this filtrate by addition of ammonium chloride, neutralization with ammonia, and addition of ammonium sulphide in excess will contain the following elements:

a. In the form of sulphides: Cobalt, nickel, manganese, iron, zinc, uranium, thallium, indium, gallium.

b. In the form of hydroxides: Aluminium, beryllium, thorium, zirconium, yttrium, cerium, lanthanum, didymium, chromium, titanium, tantalum, niobium.*

If it is now supposed that all these elements are in the precipitate, and an attempt is made, on the strength of their behavior with various precipitants, to devise a course for separating them, it will be found at once that this task is an exceedingly difficult one, particularly since many of these metals, when they are in solution with each other, behave otherwise with precipitants than when they are present alone. Now, since the case that all the members of the third and fourth groups are contained in the precipitate produced by ammonia and ammonium sulphide would never occur in reality, and since every one who desires to undertake a thorough examination of the rarer elements of the third group cannot avoid making a careful study of the newer publications relating to this domain, the authors of which I have already mentioned in the foot-note to § 117, I shall refrain from setting forth a course embracing all these elements, and limit myself to giving the most important methods of separation, which permit the separation of smaller or larger groups of the elements under consideration, and thus make them accessible for further examination.

1. The following method may be used for the separation of TANTALIC, NIOBIC, and TITANIC ACIDS: Roast the precipitate obtained by ammonia and ammonium sulphide, then fuse perseveringly in a platinum crucible with *potassium disulphate;* let the fused mass cool, soak in cold water, digest for some time without application of heat, and filter the solution from the residue. The RESIDUE, which contains the acids of tantalum and niobium, and may also contain silicic acid and a little undissolved ferric oxide and chromic oxide, gives, on fusion with *sodium hydroxide* and some *potassium chlorate*, a mass out of which dilute solution of soda will dissolve chromate and silicate of sodium, leaving undissolved, with the ferric oxide, sodium tantalate and niobate, which are insoluble in solution of caustic soda. The separation of niobic and tantalic acids is best accom-

* Of niobic acid, only the part redissolved in the precipitation by hydrochloric acid, and in washing the resulting precipitate, can be present here.

plished by converting the metals into double potassium fluorides. In regard to this, and in relation to further testing, see §§ 119 and 120.

Treat the acid SOLUTION containing the titanium, or at least the greater part of it, together with the other metals of the third and fourth groups, with hydrogen sulphide, to reduce any ferric salts; dilute largely, heat to boiling and keep boiling for some time, while conducting carbon dioxide into the fluid. The titanic acid present in the solution is separated by this means as a white precipitate, which may possibly contain zirconia also.

2. If the filtrate obtained after separating the tantalic, niobic, and titanic acids, or a solution free from these acids, is precipitated, after oxidizing any ferrous salt present by boiling with nitric acid, with *ammonia* in the presence of ammonium chloride, and if the precipitate, after being washed somewhat, is dissolved in hydrochloric acid, and another precipitation is made with ammonia, this will give almost the whole of the ZINC, MANGANESE, NICKEL, COBALT, and GALLIUM in solution, while the earths are precipitated with the hydroxides of iron, indium, uranium, and chromium.

3. Gallium may be separated from ZINC, MANGANESE, NICKEL, COBALT, and IRON (in the ferrous state), by digesting the hydrochloric acid solution of the metals with *barium carbonate* in the cold. Gallium as hydroxide is precipitated by this means, while the other metals remain in solution.

4. In order to separate ALUMINIUM and BERYLLIUM, and also CHROMIUM, from IRON (in the ferric state), INDIUM, and URANIUM, as well as from the rest of the metals of the third group, treat their hydrochloric acid solution in the cold with *concentrated potassium hydroxide* solution. By this means, aluminium and beryllium, and perhaps also chromium, are obtained in solution, while the other earth metals, with iron, indium, uranium, and perhaps also chromium, are precipitated as hydroxides. If the alkaline solution is diluted, filtered, and boiled for a long time, ALUMINA remains dissolved (and may afterwards be precipitated with ammonium chloride), while any CHROMIUM present here and BERYLLIUM are precipitated as hydroxides (see § 109). The latter may be separated by fusion with sodium carbonate and potassium chlorate in the same manner in which it is customary to separate aluminium and chromium (§ 108).

5. The further separation of the metals obtained in the ammonia precipitate in 2, viz., IRON (in the ferric state), ALUMINIUM, BERYLLIUM, CHROMIUM, and URANIUM, CERIUM, LANTHANUM, and DIDYMIUM, THORIUM, YTTRIUM, and ZIRCONIUM, is well effected, according to K. F. FÖHR,* by treating the moist, washed precipitate with a concentrated solution of *oxalic acid*, by which means the iron, aluminium, beryllium, chromium, and uranium go into solution, while the oxalates of the other metals remain undissolved.

6. THORIUM may be separated from CERIUM, LANTHANUM, and DIDYMIUM, as well as from YTTRIUM, by treating the oxalates with a boiling, concen-

* Private communication of Sept. 2 1881, partly based upon the directions in WILL's "Tafeln zur qualitativen Analyse."

trated solution of *ammonium oxalate*, diluting, and after cooling, filtering off the undissolved oxalates of the last four elements mentioned. The thoria may be obtained by evaporating the solution, and igniting the residue (R. BUNSEN).

7. ZIRCONIUM and THORIUM (and the metals of CERITE also) may be separated from YTTRIUM (as well as from BERYLLIUM and ALUMINIUM) by means of *potassium sulphate*. To the neutral or scarcely acid solution, add normal potassium sulphate in crystals, boil, let it stand for 12 hours, filter, and, with a solution of potassium sulphate, wash the resulting precipitate of the potassium double sulphates of zirconium and thorium (and of the metals of cerite). From the solution, ammonia precipitates yttrium (beryllium and aluminium) hydroxides, the last two of which may be separated from yttrium by means of oxalic acid (compare 5). If the precipitate of potassium double sulphates is repeatedly boiled with water containing a little hydrochloric acid, the potassium zirconium sulphate remains undissolved, while thorium (and the metals of cerite) go into solution, from which they may be precipitated by ammonia.

8. THORIUM and ZIRCONIUM may be separated from YTTRIUM, CERIUM, and DIDYMIUM by means of *sodium thiosulphate*, by adding it to the neutral or faintly acid solution, and heating to boiling. The former are thus precipitated, while the latter remain in solution.

9. ZIRCONIUM may be separated from THORIUM and YTTRIUM by means of *hydrofluoric acid*, which precipitates the last two, but not zirconium.

10. In regard to the separation of CERIUM from LANTHANUM and DIDYMIUM, see § 116.

11. The best way to separate INDIUM from ZINC and IRON is to make use of barium carbonate. Heat the hydrochloric acid solution first with sulphurous acid to change ferric chloride to ferrous chloride, and after cooling, allow freshly precipitated barium carbonate to act upon it, with exclusion of air. If much iron is present, the operation must be repeated. The precipitate containing indium is dissolved in hydrochloric acid, and the barium is precipitated with sulphuric acid. From the filtrate, ammonia then precipitates indium hydroxide.

12. To detect THALLIUM in the precipitate obtained with ammonia and ammonium sulphide, dissolve a part of it in boiling, dilute hydrochloric acid, treat the solution with sulphurous acid until any ferric chloride present is reduced, neutralize the free acid almost completely with ammonia, and test with *potassium iodide*. Any precipitate formed is always to be tested further by means of the spectroscope.

To §§ 231–234.

The liquid filtered from the precipitate produced by ammonium sulphide may contain not only the alkali-earth and alkali metals, but also a little NICKEL, and, moreover, VANADIC ACID, and also that part of the TUNGSTIC ACID which has not been precipitated at first with hydrochloric acid.

The last three are present as sulphides dissolved in the excess of ammonium sulphide, and are precipitated as such if the liquid is just acidified with acetic or hydrochloric acid. If the precipitate is filtered off, washed, dried, fused with sodium carbonate and potassium nitrate, and the mass is heated with water, nickel oxide remains behind, while potassium (or sodium) vanadate and tungstate dissolve. From this solution, vanadic acid may be precipitated with solid ammonium chloride, while the tungstic acid may be precipitated by evaporating with hydrochloric acid, and treating the residue with water. The two acids may be examined further by §§ 133 and 161.

In regard to deciding the question whether any alkali metals are present, attention may again be called here to the fact that care should be taken in heating a portion of the residue obtained by evaporation, because a small residue may easily be overlooked if the heat has been raised sufficiently to melt it.

Explanations in regard to the detection of LITHIUM, CÆSIUM, and RUBIDIUM may be found in § 98, and, in connection with the analysis of mineral waters, in **259** and **260**.

To § 235.

If, in an analyis, there is occasion to take hydrofluosilicic acid into consideration, it is to be noticed that the precipitate resulting in **175**, *b*, may contain barium silicofluoride. It is advisable to test for this in the first place by the aid of the microscope with a magnifying power of about 140 to 200, by examining a sample of the precipitate directly, and again after the addition of a drop of dilute hydrochloric acid, which dissolves any barium phosphate, oxalate, etc., that may be present. The crystals of barium silicofluoride, which are shaped like a whetstone, may be often seen even before the treatment with hydrochloric acid, but more easily afterwards.

For making a chemical test, a portion of the precipitate left after the *careful* addition of hydrochloric or nitric acid (barium silicofluoride is somewhat soluble in the acids) is then heated with sulphuric acid in a stream of air, according to § 176, 6.

If barium silicofluoride is found in the part of the precipitate of barium salts which is insoluble in hydrochloric or nitric acid, another portion of the precipitate must be tested for sulphuric acid. This is accomplished by igniting a portion, triturating the residue, and heating it with hydrochloric acid of 1.12 sp. gr. The barium fluoride resulting from the ignition of barium silicofluoride then dissolves, while any barium sulphate present remains behind, and may be further examined according to § 170, 6.

To §§ 237 and 239.

In order that the course may not be too complicated, the case is not considered in §§ 237 and 239, where small amounts of silicic acid are to be detected in the presence of considerable amounts of calcium fluoride or of some other fluoride. If this case occurs, as frequently happens in the analysis of fluorine minerals, the silicic acid might be entirely overlooked in proceeding according to the process given in **183, 10, and 194**, or **208** and **210**, because the silicon may completely volatilize as silicon fluoride when the alkaline solution of the fusion is acidified with hydrochloric acid and evaporated. In the analysis of substances containing fluorine, therefore, in order to separate silicic acid, treat the alkaline solution of the fusion (made according to **194** or **208**) with ammonium carbonate, heat (with the replacement of the ammonium carbonate lost by evaporation), filter, mix the filtrate with a solution of zinc oxide in aqueous ammonia, for the purpose of separating the remainder of the silicic acid, evaporate until all the ammonia has escaped, and filter. Silicic acid may then be separated from the precipitate produced by ammonium carbonate by evaporating with hydrochloric acid, and from the precipitate produced by zinc oxide in ammonia, preferably by evaporating with nitric acid.

If the rare elements are taken into account in § 239. the number of bodies which may remain undissolved on treating a substance with water, hydrochloric acid, nitric acid, and aqua regia, is much enlarged. The following bodies, more especially, are either always, or in the ignited state, or in certain combinations, insoluble or slowly and sparingly soluble in acids:

The oxides of beryllium, thorium, and zirconium ; cerium sesquioxide; titanic, tantalic, niobic, molybdic, and tungstic oxides ; rhodium, iridium, osmium, and ruthenium.

When, in the systematic course of analysis, **208** has been reached, fuse the substance, free from silver, lead, and sulphur, with sodium carbonate and some nitrate, extract the fused mass repeatedly with hot water, and, if a residue is left, fuse this a long time, in a silver crucible, with potassium hydroxide and nitrate, and again treat the fused mass repeatedly with water. The alkaline solutions, which may be examined separately or together, may contain beryllium, a portion of the titanic acid, tantalic, niobic, molybdic, tungstic, perosmic, and ruthenic acids, and a portion of any iridium present.

If the residue left undissolved by the preceding operation is fused with potassium disulphate, and the fused mass treated with water, the thorium, zirconium, cerium, the remainder of the titanium, and the rhodium will dissolve.

A residue left by the last operation may consist of platinum ore metals, and should be mixed with sodium chloride, and ignited in a stream of chlorine.

With respect to the separation and detection of the several elements that have passed into the different solutions, the requisite directions and instructions have been given in the notes to §§ 225–234, and also in Part I, Section III.

To § 240.

The analysis of cyanogen compounds is not very easy in certain cases, and it is sometimes a difficult task even to ascertain whether a substance is really a cyanide or not. However, if the reactions of the substance upon ignition (8, *gg* and *ii*) are carefully observed, and also if it is noticed whether, upon boiling with hydrochloric acid, any odor of hydrocyanic acid is emitted (35, *γ*, and 37), the presence or absence of a cyanide will generally not remain a matter of doubt.

Above all, it must be borne in mind that the insoluble cyanogen compounds, occurring in pharmacy, etc., belong to two distinct classes, viz., they are either SIMPLE CYANIDES or COMPOUNDS OF METALS WITH FERROCYANOGEN or some other similar radical.

By boiling with concentrated hydrochloric acid, all the simple cyanides are decomposed into metallic chlorides and hydrocyanic acid. Their analysis is therefore never difficult. But the ferrocyanides, etc., to which the method described in § 240 more exclusively refers, suffer such complicated decompositions by acids that their analysis by means of these is a task not so easily accomplished. Their decomposition by caustic potash or soda is far more simple. The alkali yields its hydroxyl to the metal combined with the ferrocyanogen, etc., the hydroxide or oxide thus formed precipitates, and the potassium or sodium forms with the liberated radical, soluble ferrocyanide, cobalticyanide, etc., of potassium or sodium. However, several hydroxides are soluble in an excess of potassium or sodium hydroxide, as those of

lead, zinc, etc. If, therefore, zinc potassium ferrocyanide, for instance, is boiled with solution of caustic potash, it dissolves completely, and we may assume that the solution contains potassium ferrocyanide and zinc hydroxide dissolved in potassium hydroxide. If an acid were added to this solution, of course simply the original precipitate of zinc potassium ferrocyanide would be again obtained, and consequently the operation would be of no avail. To prevent this failure, hydrogen sulphide is conducted into the alkaline solution, but only until the precipitable metals are completely thrown down, and not until the solution smells of hydrogen sulphide (compare the foot-note under **216**). This serves to convert into sulphides all the heavy metals which the alkali holds in solution as hydroxides. Those sulphides which are insoluble in caustic alkalies (those of lead, zinc, etc.) precipitate, while those which are soluble in sodium or potassium sulphides, that is, the metallic sulphides of the sixth group, and besides, any mercuric sulphide present here, remain in solution. To effect the detection of these also, the fluid is now acidified, and, if necessary, more hydrogen sulphide is conducted into it.

In the filtrate from the hydroxides and sulphides are still those metals which form radicals with cyanogen, and also any aluminium present, which would have dissolved in the original treatment with caustic alkali, and would not have been separated. Finally, the other acids must be tested for here. It is therefore directed to divide the solution into two parts, and to test one for acids, and the other for aluminium and those metals which form radicals with cyanogen. The prescribed heating of this second part with concentrated sulphuric acid has the effect of decomposing the cyanogen compounds and converting the metals into sulphates which remain behind (H. Rose.*)

If it is merely wished to examine for metals in simple or compound cyanides, and for that purpose to destroy the cyanogen compound, it will suffice to heat the powdered substance in a platinum dish with concentrated sulphuric acid diluted with a little water, till almost all the free acid is driven off. The residue will consist of sulphates, which are to be dissolved in hydrochloric acid and water.

* Zeitschr. f. analyt. Chem., 1, 194.

The reason why ferrocyanides and similar compounds which have been fully washed with water require to be tested for alkalies, is because alkali-metal ferrocyanides, etc., are often precipitated along with insoluble ferrocyanides, etc., and cannot be removed by washing; also because there are not a few compounds insoluble in water which contain heavy metals and alkali metals in chemical combination with ferrocyanogen, etc.

APPENDIX I.

Deportment of the most important Alkaloids with Reagents, and Systematic Method of effecting their Detection.

§ 266.

The detection and especially the separation of the alkaloids is far more difficult than the detection and separation of most inorganic bases. In many cases, the combinations in which an alkaloid can be separated from others are not sufficiently insoluble to allow of complete separation. In other cases, only the outward appearance of a reaction is known, and not its cause; consequently the conditions which may modify it are often unknown, while many alkaloids are as yet scarcely known to have any characteristic reaction. If these statements apply to the pure alkaloids, they apply much more strongly to the alkaloids which are not completely pure, such as are often obtained when they are separated from food, parts of dead bodies, etc.

However, in order to furnish a guide for practice in this kind of analytical experiments, for young chemists, and particularly for pharmaceutists, for whom the subject has an especial interest, this appendix is added, but it will be limited to the most important and the most commonly used alkaloids, including the following: Nicotin, coniin, morphin, cocain, narcotin, quinin, cinchonin, strychnin, brucin, veratrin, and atropin.

If the student has learned to detect and to separate these, he will then be in a position to widen the range of alkaloids easily.

This appendix will be divided into the following sections:

A. General reagents for the alkaloids.

B. Properties and reactions of the individual alkaloids,

arranged in groups according to their analytical characteristics.

C. Properties and reactions of the individual non-nitrogenous bodies which are allied to the alkaloids as poisons or are employed in their adulteration, namely, salicin, digitalin, and picrotoxin.

D. Systematic course for the detection of the alkaloids, etc., taken into consideration here:

a. When only one is assumed to be present.

b. When several or all are assumed to be present.

c. When other organic substances are present.

A. General Reagents for the Alkaloids.

§ 267.

By general reagents for the alkaloids are meant reagents by which they are all or nearly all precipitated. These are well suited to test for the presence of an alkaloid in a fluid, and may serve to separate alkaloids from their solutions, but they cannot be employed to distinguish individual alkaloids except in a subordinate degree. The reactions take place with certainty, however, only in the pure solutions of the alkaloids; for gum-arabic and other similar bodies interfere with them. Such interfering, foreign, organic substances are therefore to be removed, if need be, by dialysis, before applying the reactions (J. Lefort and P. Thibault).

The most important of these general reagents are the following:

Hydrochloroplatinic acid, a solution of iodine in potassium iodide (Wagner*), potassium mercuric iodide (v. Planta†), potassium cadmium iodide (Marmé‡), potassium bismuth iodide (Dragendorff §), phosphomolybdic acid (de Vrij, Sonnenschein ‖), phosphoantimonic acid (Fr. Schulze ¶), phosphotungstic acid (Scheibler**), and picric acid (H. Hager††).

* Zeitschr. f. analyt. Chem., **4**, 387.

† "Verhalten der wichtigsten Alkaloide gegen Reagentien," Heidelberg, 1846.

‡ Zeitschr. f. analyt. Chem., **6**, 123.

§ *Ibid.*, **5**, 406.

‖ Ann. d. Chem. u. Pharm., **104**, 47.

¶ *Ibid.*, **109**, 179.

** Zeitschr. f. analyt. Chem., **12**, 315.

†† Pharmac. Centralhalle, 10r Jahrg., 131.

With the hydrochlorides of the alkaloids, HYDROCHLOROPLATINIC ACID forms compounds analogous to ammonium platinic chloride. Some of these compounds are difficultly soluble in water, while some are rather easily soluble. They are best obtained and most completely separated by mixing the solutions with a sufficient quantity of hydrochloroplatinic acid, evaporating nearly to dryness, and treating the residue with alcohol. The compounds have a yellow color of various shades, some are crystalline, some flocculent, and in general they are more soluble in hydrochloric acid than in water.

A solution of IODINE in POTASSIUM IODIDE (containing 12.7 g of free iodine in 1 liter) precipitates the solutions of the salts of all the alkaloids. The precipitates are brown and flocculent. Their formation and separation is assisted by acidifying with sulphuric acid. By washing the precipitate, dissolving it in solution of sulphurous acid, and evaporating on the water-bath to remove the excess of the latter and the hydriodic acid, the alkaloid will remain in combination with sulphuric acid. If the precipitate was separated from a fluid containing a quantity of other organic substances, before proceeding as just stated, dissolve it in a dilute solution of sodium thiosulphate, filter, reprecipitate with iodine solution, and then proceed as directed above.*

POTASSIUM MERCURIC IODIDE precipitates solutions of the salts of all the alkaloids. The precipitates are white or yellowish-white, insoluble in water and dilute hydrochloric acid.

POTASSIUM CADMIUM IODIDE † precipitates even very dilute solutions of salts of the alkaloids after acidification with sulphuric acid. All the precipitates are at first flocculent and white, but some of them soon become crystalline. They are insoluble in ether, readily soluble in alcohol, less soluble

* By dissolving the brownish-red precipitate, produced by mixing the iodine solution with a salt of strychnin, in alcohol containing sulphuric acid, and evaporating, prismatic crystals of a strong polarizing power, consisting of the sulphuric acid salt of iodostrychnin, will be obtained (DE VRIJ and VAN DER BURG, Jahresber. von LIEBIG u. KOPP, 1857, 602). Concerning jodoquinin sulphate, see § 275, 7.

† Prepared by saturating a boiling, concentrated solution of potassium iodide with cadmium iodide, and adding an equal volume of cold saturated solution of potassium iodide. The concentrated solution keeps well, but not the dilute.

in water, and readily soluble in excess of the precipitant. They have a tendency to decompose by long standing. The alkaloids may be obtained from the undecomposed precipitates by mixing with an alkali-metal carbonate or hydroxide and water, and shaking with a solvent which is adapted for taking up the alkaloid (benzol, amyl alcohol, ether, or the like).

POTASSIUM BISMUTH IODIDE * added drop by drop to solutions of salts of the alkaloids acidified with sulphuric acid (10 cc of the alkaloid solution and 5 drops of concentrated sulphuric acid) almost immediately produces flocculent, orange precipitates in the case of nicotin, coniin, morphin, cocain, narcotin, quinin, and cinchonin, strychnin, brucin, atropin, and most other alkaloids. Veratrin, on the other hand, gives only a faint turbidity. The precipitates formed with the salts of the first-named alkaloids agglutinate together to some extent when heated; but dissolve by long-continued boiling, and separate again for the most part on cooling. None of the precipitates are crystalline. The alkaloids may be separated from the precipitates in the same manner as those produced by potassium cadmium iodide.

PHOSPHOMOLYBDIC ACID SOLUTION † is precipitated by the solutions of all alkaloids, even when their quantity is very

* Prepared, according to DRAGENDORFF, as follows: In a tube of difficultly fusible glass sealed at one end, heat 32 parts of bismuth sulphide with 41.5 parts of iodine, collect the bismuth iodide in a receiver, purify it by resublimation, heat it with solution of potassium iodide, filter hot, and add to the solution an equal volume of a cold saturated solution of potassium iodide. The concentrated, orange-colored solution keeps well, but not the dilute. On mixing 10 cc of water with 5 drops of concentrated sulphuric acid and adding 1 or 2 drops of the reagent, no turbidity should occur. FRON (Chem. Centralbl., 1875, p. 263) prepares the reagent by suspending 1.5 g of freshly precipitated, unwashed, basic bismuth nitrate in 20 g of water, heating to boiling, adding 7 g of potassium iodide, and at last 20 drops of hydrochloric acid. The solution to be tested for alkaloids by means of this liquid should contain a few drops of hydrochloric acid, as otherwise the reagent is decomposed by water.

† Prepared as follows: Precipitate the nitric acid solution of ammonium molybdate with sodium phosphate, wash the precipitate well, suspend it in water, and warm with addition of sodium carbonate to complete solution. Evaporate to dryness, ignite the residue until ammonia is completely removed, and if reduction has taken place, moisten with nitric acid, and ignite again. Warm the residue with water, and dissolve by adding nitric acid in considerable excess. One part of the residue should make 10 parts of solution. The golden-yellow solution must be protected from ammoniacal fumes.

minute. The precipitates are amorphous, light yellow, ochreous or brownish yellow, insoluble or very difficultly soluble at the ordinary temperature in water, alcohol, ether, and dilute mineral acids, with the exception of phosphoric acid; but they are most insoluble in dilute nitric acid, especially when it contains some of the reagent. Acetic acid, also, is almost without action in the cold, but when hot it has a solvent action. The precipitates dissolve with ease in the hydroxides and carbonates of the alkali metals, generally with separation of the alkaloids. Upon prolonged action, they are decomposed also by alkali earths, silver and lead oxides and carbonates, with the separation of the alkaloids. The alkaloids set free may be removed by shaking with ether, amyl alcohol, benzol, or the like.

PHOSPHOANTIMONIC ACID, obtained by dropping antimonic chloride into aqueous phosphoric acid, also precipitates ammonia and most of the alkaloids (but not caffein). The reactions are delicate, but they are generally less delicate than those produced by phosphomolybdic acid, especially in the case of nicotin and coniin, although the phosphoantimonic acid is more delicate in one single instance (namely, for atropin). The precipitates are usually flocculent and whitish, but the brucin precipitate is rose-colored. On heating, this dissolves, and on cooling, it separates again from the fluid, which retains an intense crimson color.

PHOSPHOTUNGSTIC ACID* precipitates the solutions of all the alkaloids. The precipitates are white and flocculent. The delicacy of the reactions is extreme. Acid solutions containing only 1 part of strychnin in 200,000, or 1 part of quinin in 100,000, are rendered distinctly turbid. If the flocks settle to the bottom of the vessel after twenty-four hours, they may be filtered and washed with slightly acidified water without passing through the filter. The precipitates are decomposed by caustic lime or baryta, with the formation of insoluble phosphotungstates, and the separation of the alkaloids.

PICRIC ACID precipitates almost all the alkaloids, even from

* To prepare this reagent, mix a solution of ordinary sodium tungstate with some phosphoric acid.

solutions containing a large excess of sulphuric acid. The precipitates, which are crystalline or soon become so, are yellow, and usually insoluble in an excess of the precipitant, and are formed, with most of the alkaloids, even in very dilute solutions. The exceptions will be mentioned in connection with the separate alkaloids.*

B. Properties and Reactions of the individual Alkaloids.

a. Volatile Alkaloids.

The volatile alkaloids are liquid at the common temperature, and may be volatilized in the pure state as well as when mixed with water. They are accordingly obtained in the distillate when their salts are distilled with strong fixed bases and water. Their vapors, when brought in contact with those of volatile acids, form a white cloud.

§ 268.

1. Nicotin, $C_{10}H_{14}N_2$.

1. Nicotin occurs in the leaves and seed of tobacco. In its pure state, it forms a colorless, oily liquid, to which the action of air imparts a yellowish or brownish tint. Its specific gravity compared with water of 4° is 1.01837 at 10.2°, and 1.01101 at 20° (Landolt). It boils at 247° in an atmosphere of hydrogen without decomposition (Landolt); when heated to boiling in contact with air, it is partly decomposed. It mixes with water in all proportions. Potassium and sodium

* To the general reagents which precipitate the alkaloids, the following that give more or less characteristic colorations, and sometimes precipitations with many alkaloids, may be added: Phosphoric acid; sulphuric acid with subsequent addition of caustic potash; sulphuric acid and potassium nitrate (C. Arnold, Zeitschr. f. analyt. Chem., **23**, 228); bromine-water (Bloxam, *ibid.*, **25**, 247); a solution of potassium chromate in sulphuric acid, prepared hot (Luchini, *ibid.*, **25**, 565); potassium permanganate and sulphuric acid (Wenzell, *ibid.*); chromic acid; chromic acid with subsequent addition of hydrochloric acid; normal potassium chromate (Mezger, *ibid.*, **29**, 107); ammonium selenite dissolved in sulphuric acid (Ferreira da Silva, Chem. Centralbl., 1891, II, p. 228); furfurol and sulphuric acid (P. Woltering, *ibid.*, 1892, I, p. 1008).

hydroxides separate it from the solutions. It is easily dissolved by alcohol, ether, amyl alcohol, and petroleum-ether.

Nicotin has a peculiar, disagreeable, somewhat ethereal, tobacco-like odor. On heating, it gives off a stupefying odor of tobacco. It has an acrid, pungent taste, and very poisonous properties. Dropped on paper, it makes a transparent stain, which slowly disappears; while it turns turmeric-paper brown, and litmus-paper blue. Concentrated aqueous solution of nicotin shows these reactions more distinctly than the alkaloid in the pure state.

2. Nicotin has the character of a rather strong base, precipitating metals as hydroxides from their solutions, and forming salts with acids. The salts are not volatile or scarcely so, freely soluble in water and alcohol, insoluble in ether, with the exception of the acetate, and insoluble in amyl alcohol, chloroform, benzol, as well as petroleum-ether. They are odorless, but taste strongly of tobacco, and part of them are crystallizable. Their solutions may be evaporated at a moderate temperature without any considerable loss of nicotin. The hydrochloric acid salt of nicotin forms a deliquescent, crystalline mass, which, upon evaporating its solution, is partly decomposed into its constituents and volatilized (A. PINNER). When distilled with solution of potassium hydroxide, the salts give a distillate containing nicotin. By neutralizing this with oxalic acid, and evaporating, nicotin oxalate is produced, which may be freed from any admixture of ammonium oxalate by means of alcohol, in which the former salt is soluble, the latter insoluble.

3. If an aqueous solution of nicotin, or a solution of a nicotin salt mixed with solution of caustic potash or soda, is shaken with *ether* or *petroleum-ether*, the nicotin is dissolved by these solvents. If the latter are then allowed to evaporate on a watch-glass at 20° or 30°, the nicotin remains behind in drops and streaks, and on warming the watch-glass, it volatilizes in white fumes having a strong odor. If a solution of hydrochloric acid in ether is added to the evaporating liquid, nicotin hydrochloride remains as a yellow, amorphous mass, which becomes crystalline only after long standing.

4. In not too dilute aqueous solutions of nicotin or its salts, *hydrochloroplatinic acid* produces whitish-yellow precipi-

tates, which are flocculent at first. On heating the fluid containing the precipitate, the latter dissolves, but upon continued application of heat it very speedily separates again in the form of an orange-yellow, heavy crystalline powder, which, under the microscope, appears to be composed of roundish crystalline grains. If a rather dilute aqueous solution of nicotin, containing hydrochloric acid in excess, is mixed with hydrochloroplatinic acid, the fluid at first remains clear. After some time, however, the salt separates in small crystals (oblique four-sided prisms), clearly discernible with the naked eye. An alcoholic solution of nicotin containing some free hydrochloric acid gives a yellow precipitate at once with hydrochloroplatinic acid. The double salt thus obtained forms a finely granular powder.

5. *Hydrochlorauric acid* added in excess to aqueous solutions of the alkaloid or its salts produces a reddish-yellow, flocculent precipitate, sparingly soluble in hydrochloric acid.

6. Solution of *iodine in potassium iodide* and water, when added in small quantity to an aqueous solution of nicotin, produces a yellow precipitate, which after a time disappears. Upon further addition of the iodine solution, a copious scarlet-brown precipitate separates, and a similar precipitate is produced also in solutions of nicotin salts. This precipitate also disappears after a time.

7. In an aqueous solution of nicotin, solution of *tannic acid* produces a copious, white precipitate, which dissolves upon the addition of some hydrochloric or dilute sulphuric acid.

8. If an aqueous solution of nicotin is added to an excess of *mercuric chloride* solution, an abundant, flocculent, white precipitate is formed, which is soluble in hydrochloric acid as well as in ammonium chloride solution. The neutral solutions of nicotin hydrochloride, but not those containing an excess of acid, also give a white precipitate with mercuric chloride.

9. If an aqueous or alcoholic solution of nicotin is mixed with *silver nitrate*, there is produced after some time a slight, brown coloration of the liquid, which slowly becomes stronger, and upon long standing a brownish-black precipitate is deposited.

10. *Concentrated sulphuric acid*, and *nitric acid* of 1.2 sp. gr.,

dissolve nicotin, in the cold, without coloration, but cold *nitric acid* of 1.3 sp. gr. dissolves it to a red liquid.

11. If 1 drop of nicotin is gently warmed with 3 or 4 drops of *hydrochloric acid* of 1.12 sp. gr., a pale brownish solution is obtained. If, after cooling, a drop of nitric acid of 1.4 sp. gr. is added to this, the liquid becomes colored violet-red, gradually becoming red.

12. If a solution of nicotin in ether, prepared in the proportion of about 1 : 100, is mixed with a solution of *iodine in ether*, a brownish-red, tarry oil separates out, which gradually solidifies in a crystalline condition. From the pale, brownish-yellow solution, above this, upon standing, there are formed long, transparent, ruby-red, needle-shaped crystals, which are iridescent in reflected light (ROUSSIN'S crystals).

13. *Picric acid*, added in excess to an aqueous nicotin solution or to a solution of a neutral nicotin salt, produces a yellow precipitate. The precipitate is crystalline, or soon becomes so. It is soluble in hydrochloric acid.

14. According to DRAGENDORFF and ZALEWSKY, in testing .1 cc of a neutral nicotin salt, the *general reagents* for alkaloids show the following delicacy: Hydrochloroplatinic acid, 1 : 5000; hydrochlorauric acid, 1 : 10,000; phosphomolybdic acid, 1 : 40,000; potassium bismuth iodide, 1 : 40,000; potassium mercuric iodide, 1 : 15,000; mercuric chloride, 1 : 1000; tannic acid, 1 : 500; iodine in potassium iodide, 1 : 3000.*

§ 269.

2. CONIIN, $C_8H_{17}N$.

1. Coniin occurs in the seed, especially when still unripe, but also in all other parts of the spotted hemlock. It forms a colorless oily liquid of .886 sp. gr., to which the action of the air imparts a brown tint. In the pure state it boils at 168.5°, when heated in a stream of hydrogen gas it distils over unaltered, but when distilled in vessels containing air, it turns

* As regards further reactions for nicotin, compare OECHSNER DE CONINCK, Chem. Centralbl., 1887, pp. 357 and 667; also VAN SENUS, *ibid.*, 1892, I, p. 1008.

brown and suffers partial decomposition. With aqueous vapors, it distils over freely. It dissolves sparingly in water, 90 parts of water of average temperature dissolving 1 part of coniin. The solution becomes turbid on warming, but clear again on cooling. Coniin is miscible in all proportions with alcohol, and also dissolves easily in ether, petroleum-ether, and volatile and fatty oils. It dissolves less readily in chloroform. The aqueous and alcoholic solutions manifest a strong alkaline reaction. Coniin volatilizes even at the ordinary temperature to a considerable degree, and has a very strong, pungent, repulsive odor, which affects the head, and which resembles that of the excrement of mice.* It is very poisonous.

2. Coniin is a strong base; it accordingly precipitates metallic salts in a manner similar to ammonia, and forms salts with acids. The salts of coniin are soluble in water and in alcohol, insoluble in petroleum-ether, and insoluble or almost insoluble in ether. Coniin forms dense white clouds with volatile acids. Coniin hydrochloride crystallizes readily, and the smallest quantity of coniin brought in contact with a trace of hydrochloric acid yields almost immediately a corresponding quantity of non-deliquescent rhombic crystals (TH. WERTHEIM). Coniin hydrochloride dissolves in absolute alcohol (difference and means of separation from ammonium chloride, W. LENZ). From solutions of the sulphuric acid salt of coniin, needle-like crystals are first obtained, which afterwards become large and leaf-like (DRAGENDORFF). The salts when dry give off no odor of coniin, and when moistened, only a slight odor, but this becomes very strong at once when sodium hydroxide solution is added, and upon distilling, a distillate containing coniin is obtained in the last case. On neutralizing this with oxalic acid, evaporating to dryness, and treating the residue with alcohol, coniin oxalate is dissolved, while any ammonium oxalate that may be present is left undissolved. As coniin is only sparingly soluble in water, and dissolves with still greater difficulty in solutions of alkalies, a concentrated solution of a coniin salt turns milky upon addition of solution of caustic soda. The minute drops which separate unite gradually, and collect on the surface.

* According to ZALEWSKY, the mouse-like odor does not belong to the pure coniin, but to that which is not quite pure, as it is usually obtained.

3. If an aqueous solution of a salt of coniin is shaken with *caustic soda solution* and *ether* or *petroleum-ether*, the coniin is taken up by the solvent. If this is then allowed to evaporate on a watch-glass at 20° or 30°, the coniin is left in yellowish, oily drops.

4. In somewhat concentrated solutions of coniin hydrochloride, *hydrochlorauric acid* produces a yellowish-white precipitate, insoluble in hydrochloric acid.

5. *Mercuric chloride* gives with coniin a white precipitate, soluble in hydrochloric acid.

6. In aqueous and alcoholic solutions of coniin, *silver nitrate* produces at once a grayish-brown precipitate.

7. *Hydrochloroplatinic acid* does not precipitate even concentrated solutions of coniin hydrochloride, and even upon addition of alcohol, no precipitate is formed (essential difference from nicotin.)

8. If water is placed upon coniin, and *chlorine-water* is added, an abundant white precipitate is formed, which is easily soluble in hydrochloric acid (difference from nicotin).

9. If coniin is covered with a little water, and a concentrated solution of *picric acid* is added, a yellow precipitation results, while a solution which is at all dilute is not precipitated.

10. With a solution of *iodine* and *potassium iodide*, and with *tannic acid*, coniin behaves like nicotin.

11. Coniin dissolves without coloration in cold concentrated sulphuric acid and in nitric acid of 1.4 sp. gr.

12. By the use of .1 cc of a neutral coniin sulphate solution, DRAGENDORFF and ZALEWSKY observed the following degrees of delicacy for the *general reagents* for alkaloids: Phosphomolybdic acid, 1 : 5000; potassium bismuth iodide, 1 : 6000; potassium mercuric iodide, 1 : 1000; tannic acid, 1 : 100; iodine with potassium iodide, over 1 : 10,000.*

* In regard to another reaction for coniin, compare VAN SENUS, Chem., Centralbl., 1892, I, p. 1008.

Recapitulation and Remarks.

§ 270.

The volatile alkaloids are most easily recognized when pure, and the object of the analyst must accordingly be to obtain them in that state. The way of effecting this is the same for nicotin as for coniin, and has already been given in the foregoing paragraphs, viz., distil the aqueous solution containing them, with addition of caustic soda solution, in a current of hydrogen; neutralize the distillate with oxalic acid, evaporate, dissolve in alcohol, evaporate the solution, treat the residue with water, add caustic soda solution, shake the mixture with ether or petroleum-ether, and let the solvent evaporate at about 20°. Coniin is distinguished from nicotin chiefly by its odor, its sparing solubility in water, the behavior of the aqueous solution upon heating, the rapid crystallization, the crystalline form and optical properties of its hydrochloric acid salt, and also by its deportment with silver nitrate, hydrochloroplatinic acid, chlorine-water, and picric acid. Nicotin is characterized by its deportment upon heating with hydrochloric acid and subsequently adding nitric acid, but especially by its behavior with ethereal iodine solution. It should be noticed further that the general reagents for alkaloids precipitate nicotin in much more dilute solutions than coniin.*

* In relation to the detection of coniin in the presence of nicotin, with the aid of potassium platinic iodide, compare SELMI, Ber. d. deutsch. chem. Gesellsch., 9, 195; by means of potassium platinic sulphocyanide, see I. GUARESCHI, Chem. Centralbl., 1891, II, p. 621.

b. Non-volatile Alkaloids.

The non-volatile alkaloids are solid, and cannot be distilled over with water.

FIRST GROUP.

Non-volatile alkaloids which are precipitated by caustic potash or soda from the solutions of their salts, and redissolve in an excess of the precipitant.

Of the alkaloids considered here, only morphin and cocain belong to this group.

§ 271.

1. Morphin, $C_{17}H_{19}NO_3$.

1. Morphin occurs with the alkaloids codein, thebain, papaverin, narcotin, and narcein, etc., and with meconic acid and the indifferent nitrogen-free compounds meconin and meconoisin, in opium, the dried milky juice of the green seed-capsules of the poppy (*Papaver somniferum*).* Crystallized morphin, $C_{17}H_{19}NO_3.H_2O$, usually appears in the form of colorless, brilliant, transparent needles, short rhombic prisms, or, when obtained by precipitation, as a white crystalline powder having a bitter taste. According to the recent investigations of Dieterich,† it dissolves in solvents in the following proportions: In cold water, 1 : 1250 (in hot water much more easily, about 1 : 400); in cold ethyl alcohol, 1 : 166 (much more easily at the boiling temperature); in ether, 1 : 1250; in amyl alcohol, 1 : 130 (when not crystallized and upon heating, much more easily); in benzol, 1 : 5000; in chloroform, 1 : 1660; in petroleum-ether, 1 : 5000. The solutions of morphin in hot alcohol, as well as in hot water, manifest distinctly alkaline reaction and taste bitter. Morphin is removed from the solutions by freshly ignited bone-charcoal

* In regard to the separation of the opium alkaloids, compare Pluggе, Zeitschr. f. analyt. Chem., 30, 385.

† Pharmac. Centralhalle, 1887, p. 481.

(M. J. LEFORT). Crystallized morphin loses its water of crystallization even at 90° to 100°, and by careful heating to a higher temperature, not much below 230°, the morphin may be fused and sublimed, with partial decomposition (HESSE).*

2. Morphin neutralizes acids completely, and forms with them the MORPHIN SALTS. These salts are, for the most part, crystallizable, easily soluble in water, and mostly in alcohol also. (The sulphate requires 700 parts of cold, and 144 parts of boiling alcohol of .82 sp. gr.). They are insoluble in ether, chloroform, and amyl alcohol, and possess a disagreeable, bitter taste. Freshly ignited bone-charcoal also removes the morphin from morphin-salt solutions (DRAGENDORFF). Morphin and the morphin salts are poisonous.

3. From solutions of morphin salts, generally only after some time, *potassium*, *sodium*, and *ammonium hydroxides* precipitate morphin containing water of crystallization, in the form of a white crystalline powder. Stirring and friction on the sides of the vessel under the liquid promote the separation of the precipitate. The precipitate redissolves with great readiness in an excess of potassium or sodium hydroxide, but more sparingly in ammonia. It dissolves also in ammonium chloride, and with difficulty in ammonium carbonate. On shaking a solution of morphin in caustic potash or soda with petroleum-ether, no morphin is removed from the solution, and on shaking with ether, very little of the alkaloid is taken up, while on shaking with warm amyl alcohol, however, the whole of the alkaloid passes into the latter.

4. *Potassium carbonate* and *sodium carbonate* produce the same precipitate as potassium hydroxide, sodium hydroxide, and ammonia, but fail to redissolve it upon addition in excess. Consequently, if a fixed alkali bicarbonate is added to a solution of morphin in caustic potash or soda, or if carbon dioxide is conducted into the solution, hydrous morphin separates, especially after previous boiling, in the form of a crystalline

* For the best way of subliming morphin, and for the value of the sublimate in microscopic diagnosis, see HELWIG, Zeitschr. f. analyt. Chem., 3, 43; or "Das Mikroscop in der Toxikologie," von Dr. A. HELWIG (von Zabern, Mainz, 1864). In the latter work, the subject is treated more completely, and illustrated. It may be mentioned that the alkaloid must be perfectly pure and free from all adhering substances, in order that this interesting experiment may succeed.

powder. A more minute inspection, particularly through a lens, distinctly shows this powder to consist of small acicular crystals; and when magnified 100 times, these crystals present the form of rhombic prisms.

5. In neutral solutions of morphin salts, *sodium bicarbonate and potassium bicarbonate* speedily produce a precipitate of hydrous morphin in the form of a crystalline powder. The precipitate is insoluble in an excess of the precipitants. These reagents fail to precipitate acidified solutions of morphin salts in the cold.

6. The action of strong *nitric acid* upon morphin or one of its salts, in the solid state or in concentrated solutions, produces a yellowish-red color. On addition of stannous chloride, no violet coloration occurs (difference from brucin). Dilute solutions do not change their color upon addition of nitric acid in the cold, but upon heating, they acquire a yellow tint.

7. Absolutely pure *concentrated sulphuric acid* dissolves morphin, in the cold, to a colorless liquid. If a trace of *potassium nitrate* is added to the freshly prepared solution, the latter is colored at the place of contact, sometimes at first reddish for an instant, but soon brown, and often brown at once. If, however, the solution of morphin in concentrated sulphuric acid is allowed to stand in the cold for 12 to 15 hours, or if it is heated for half an hour to 100°, or for a few moments to 150°, it undergoes an essential change. This is to be recognized by a slight, pale, dirty violet coloration of the solution itself, but especially from the fact that the cold solution, if now brought into contact with a trace of *potassium nitrate* or with a small drop of *nitric acid* of 1.2 sp. gr., upon a porcelain surface, assumes a magnificent coloration, which (according to my own observations) is sometimes first violet and then blood-red, but sometimes also blood-red at once with a tinge of brown, and with exceedingly small quantities is only pink (A. HUSEMANN).* The reaction is very characteristic, and at the same time very delicate, even though it is not quite so delicate as that of FRÖHDE (see 8, p. 676). KAUZMANN and DRAGENDORFF†

* Zeitschr. f. analyt. Chem., 3, 149, and 15, 103.

† DRAGENDORFF, "Beiträge zur gerichtlichen Chemie einzelner organischer Gifte," St. Petersburg (Schmitzdorff), 1872, p. 124.

violet-red color is obtained (PELLAGRI).* Codein gives the same reaction.

12. *Neutral ferric chloride* imparts to *concentrated* neutral solutions of morphin salts a beautiful dark blue color, which disappears upon the addition of an acid. An excess of ferric chloride also interferes with the delicacy of the reaction. For .01 g of morphin hydrochloride, dissolved in 100 to 200 cc of water, .2 cc. of a 5 per cent solution of ferric chloride suffices. By using this proportion, DRAGENDORFF † still obtained the reaction with solutions containing 1 part of the morphin salt in 1000 to 1500 parts of water. If the solution contains an admixture of animal or vegetable extractive matters, or of acetates, the color will be impure and less distinct. The delicacy of the reaction is increased by adding a little potassium ferricyanide, because this is reduced to potassium ferrocyanide (while the morphin oxidizes to oxymorphin), and causes the formation of Prussian blue (KIEFER, O. HESSE). The reaction thus modified is, of course, indicative of morphin only in the absence of other substances which have a reducing action.

13. If *iodic acid*, or *sodium iodate* and *sulphuric acid*, is added to a solution of morphin or of a morphin salt, iodine separates. In concentrated aqueous solutions, the separated iodine appears as a reddish-brown precipitate, while to alcoholic and dilute aqueous solutions, it imparts a brown or yellowish-brown color. The addition of starch paste to the fluid, before or after that of the iodic acid, considerably heightens the delicacy of the reaction, since the blue tint of the iodized starch (which appears only after some time when the morphin solution is very dilute) remains perceptible to far greater dilution than the brown color imparted by iodine. The reaction is most delicate when the iodic acid solution is mixed with starch paste and the dry morphin salt is added to the mixture. It need scarcely be mentioned that the delicacy of the reaction may also be increased by shaking with carbon disulphide in order to take out the iodine set free by the morphin. As other nitrogenous bodies (albumin, casein, fibrin, etc.) likewise reduce iodic acid, this reaction has only a

* Zeitschr. f. analyt. Chem., 17, 373. † *Loc. cit.*, p. 125.

relative value; but if *ammonia* is added after the iodic acid, the fluid becomes colorless if the separation of iodine has been caused by other substances, while the coloration becomes much more intense if it is owing to the presence of morphin (LEFORT).*

14. A solution of *ammonium vanadate in concentrated sulphuric acid* (1 : 100) is colored brown by morphin, then gradually bluish-violet, and after long standing, dark brown.

15. *Tannic acid* gives a white precipitate in aqueous solutions of morphin salts, if they are not extremely dilute. The precipitate is readily soluble in acids.

16. *Picric acid* precipitates yellow morphin picrate, from neutral, concentrated solutions of morphin salts. The precipitate dissolves upon the addition of water.

17. The most delicate of the *general reagents* for morphin are phosphomolybdic acid, potassium bismuth iodide, iodine with potassium iodide, and potassium mercuric iodide.†

§ 272.

2. COCAIN, $C_{17}H_{21}NO_4$.

1. Cocain occurs in coca leaves. From an alcoholic solution mixed with water, it crystallizes in colorless, transparent prisms. It fuses at 98°, and solidifies upon cooling to a transparent, amorphous mass, which becomes white and crystalline after some time. It tastes bitter and afterwards cooling,

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* Zeitschr. f. analyt. Chem., **1**, 134. The detection of morphin by reactions with silver nitrate also depends upon its reducing power (HORSLEY, Zeitschr. f. analyt. Chem., **7**, 485), as do those with cupric oxide in ammonia (NADLER, *ibid.*, **13**, 235).

† In regard to other reactions for detecting morphin, see PELLETIER, FLUCKIGER, Zeitschr. f. analyt. Chem., **11**, 319; NADLER, *ibid.*, **13**, 236; GROVE, SIEBOLD, *ibid*, **13**, 236; FLÜCKIGER, *ibid*, **19**, 120, and his "Pharm. Chem.," p. 373; LINDO, Zeitschr. f. analyt. Chem., **19**, 359; JORISSEN, *ibid.*, **20**, 422; VITALI, *ibid.*, **21**, 581; PALM, *ibid*, **22**, 224; GRIMAUX, *ibid*, **22**, 267; C. ARNOLD, *ibid.*, **23**, 228; A. EILOART, *ibid.*, **25**, 248; DONATH, *ibid.*, **26**, 746; VULPIUS, *ibid*, **30**, 250; PH LAFON, Chem. Centralbl., 1885, p. 627; BROCINER, *ibid.*, 1888, p 1294, and 1890, I, p. 299; LAMAL, *ibid.*, 1894, II, p. 602; CHASTAING and BARILLOT, Pharmac. Centralhalle, 1888, p. 223.

has a benumbing action, destroying the sense of feeling, and it dilates the pupil. It dissolves in 704 parts of cold water, and more abundantly in hot water. It dissolves easily in alcohol, and still more easily in ether. The solutions have an alkaline reaction (NIEMANN, LOSSEN).

2. Cocain dissolves readily in dilute acids, forming salts. Cocain hydrochloride is characterized by being easily obtained in crystals which have a very bitter taste, are permanent in the air, have a neutral reaction, are soluble in water, alcohol, and chloroform, but insoluble in ether. If a solution of cocain in an excess of dilute hydrochloric acid is shaken with ether, chloroform, petroleum-ether, or benzol, the alkaloid is not taken up by them, but it is extracted by amyl alcohol.

3. In solutions of cocain salts, *potassium* and *sodium hydroxides* produce a white precipitate which gradually dissolves in a considerable excess of the precipitant. *Ammonia* gives a white precipitate in the same manner, but the precipitate dissolves somewhat more readily in an excess of it. When the ammoniacal solution is shaken with ether, the latter extracts the cocain, and petroleum-ether behaves in the same way. Upon evaporating the solvent in the air, the alkaloid remains behind in fine needles.

4. In solutions of cocain salts, *potassium* and *sodium carbonates* produce white amorphous precipitates, which are not soluble in an excess of the precipitant, and become crystalline upon long standing. If the liquid is shaken with ether after the precipitation has been effected, the cocain is taken up.

5. *Potassium* or *sodium bicarbonate* produces no precipitate in solutions of cocain salts in the cold. Upon heating to boiling, a precipitate is formed, but it dissolves again upon cooling.

6. *Concentrated sulphuric acid* dissolves cocain to a colorless liquid in which a small amount of nitric acid gives no coloration, either directly or after heating the sulphuric acid solution to 150°. Sulphuric acid containing molybdic acid or white sugar also gives no characteristic colors.

7. Cocain separates no iodine from a dilute solution of *iodic acid*.

8. If cocain is dissolved in from .5 to 1 cc of *concentrated*

sulphuric acid and a quantity of *sodium* or *potassium iodate* is added, corresponding to about three times the amount of cocain used, and the liquid is gently warmed upon the water-bath, it is at first colored yellow, then light-green streaks appear. Upon continued heating, the whole liquid becomes grass-green and then brown.*

9. If a not too dilute cocain solution, containing little free hydrochloric acid, is mixed with a solution of *potassium chromate* or *dichromate*, a lemon-yellow precipitate of COCAIN CHROMATE is formed, which is soluble in more hydrochloric acid, as well as in much water (C. MEZGER).

10. *Tannic acid* gives a precipitate with solutions of cocain containing hydrochloric acid. The yellowish precipitate formed at first agglomerates to a resinous mass upon long standing, or at once upon shaking (NIEMANN).

11. In concentrated solutions of cocain salts, *stannous chloride* produces a dense, white, curdy precipitate, soluble in nitric acid (NIEMANN).

12. If a solution of a cocain salt is mixed with *mercuric chloride* solution, a white precipitate, soluble in hydrochloric acid, ammonium chloride, and also in alcohol, is produced (NIEMANN).

13. If cocain or one of its salts is treated in the dry state with a few drops of *nitric acid* of 1.4 sp. gr., the colorless solution is evaporated to dryness upon the water-bath, and one or two drops of *alcoholic potash* are added to the residue, there appears upon stirring a distinct odor of peppermint (FERREIRA DA SILVA).

14. If a few drops of a cocain solution are mixed with 2 or 3 cc of chlorine-water and a few drops of a 5 per cent *palladious chloride* solution are added, a beautiful red precipitate is formed (GREITTHERR).

15. If cocain is heated with *concentrated hydrochloric acid* in a *sealed tube* in the water-bath for two or three hours, the cocain decomposes into BENZOIC ACID, ECGONIN HYDROCHLORIDE, and METHYL ALCOHOL (WÖHLER and LOSSEN). Upon cooling, the benzoic acid separates in crystals if its amount is not too small.

* VITALI, by whom this reaction was first mentioned, describes the colorations somewhat differently.

16. Of the *general reagents* for the alkaloids, the most delicate for cocain are potassium iodide and iodine, potassium mercuric iodide, and phosphomolybdic acid (HELMSING).

17. In regard to the *microscopic detection* of cocain, see SONNIÉ-MORET, Chem. Centralbl., 1893, I, p. 859. *

Recapitulation and Remarks.

§ 273.

Morphin and cocain are distinguished by many reactions, of which those given in § 271, 7 to 13, are the most characteristic for morphin, while those described in § 272, 8, 9, 13, and 15, are especially characteristic for cocain. The two alkaloids may be separated by making the solution of their salts just alkaline with ammonia, and shaking with petroleum-ether, which takes up the cocain and leaves the morphin behind. When the petroleum-ether is evaporated, the cocain remains behind.

SECOND GROUP.

NON-VOLATILE ALKALOIDS WHICH ARE PRECIPITATED BY CAUSTIC POTASH FROM THE SOLUTIONS OF THEIR SALTS, BUT DO NOT REDISSOLVE TO ANY CONSIDERABLE EXTENT IN AN EXCESS OF THE PRECIPITANT, AND ARE PRECIPITATED BY SODIUM BICARBONATE EVEN FROM ACID SOLUTIONS, if the latter are not diluted in a larger proportion than 1: 100; Narcotin, quinin, cinchonin.

§ 274.

1. NARCOTIN, $C_{22}H_{23}NO_7$.

1. Narcotin accompanies morphin in opium (§ 271). Crystallized narcotin usually forms colorless, brilliant, right rhombic prisms, or, when precipitated by alkalies, a white, loose, crystalline powder. It is scarcely soluble (1 : 5000) in

* In reference to other reactions for cocain, compare E. SCHELL, Zeitschr. f. analyt. Chem., 30, 264; F. GIESEL, Chem. Centralbl., 1887, p. 1448; SCHAERGES, *ibid.*, 1893, II, p. 888.

cold water, and only slightly in hot water. Alcohol and ether dissolve it in the proportion of 1 : 190 and 1 : 178, respectively, in the cold, but somewhat more readily upon heating. Chloroform dissolves it very easily (1 : 4), amyl alcohol with difficulty (1 : 415), benzol more readily (1 : 12), and petroleum-ether scarcely at all (1 : 5000).* Solid narcotin is tasteless, but the alcoholic and ethereal solutions are intensely bitter. Narcotin does not alter vegetable colors. It fuses at 176°.

2. Narcotin dissolves readily in acids, combining with them to form salts. These salts invariably have an acid reaction. Those with weak acids are decomposed by a large amount of water, and if the acid is volatile, even upon simple evaporation. Most of the salts of narcotin are amorphous, soluble in water, alcohol, and ether, and have a bitter taste. Narcotin does not dissolve in water which is slightly acidified with acetic acid. If solutions of narcotin salts are shaken with chloroform, the narcotin is taken up by the solvent, even if free acids are present (DRAGENDORFF). Benzol, amyl alcohol, and petroleum-ether extract no narcotin from acid solutions.

3. From solutions of narcotin salts, *alkali-metal hydroxides, carbonates*, and *bicarbonates* precipitate narcotin at once, as a white powder, which is shown, upon being magnified 100 times, to be an aggregation of small, needle-shaped crystals. The precipitate is insoluble in an excess of the precipitants. If a narcotin-salt solution is treated with ammonia, and then mixed with ether in not too small amount, the alkaloid dissolves in the ether, and two clear layers of liquid are obtained. If a drop of the ethereal solution is allowed to evaporate upon a glass plate, and the residue is examined with a magnifying power of 100, it is seen to consist of distinct, elongated, and partly of pointed, crystals.

4. *Nitric acid* of 1.4 sp. gr. dissolves narcotin, with the production of heat and the evolution of nitrous fumes, to a reddish-yellow liquid. Upon heating this, more nitrous fumes escape and the liquid becomes yellow.

5. *Concentrated sulphuric acid* dissolves narcotin, first with a faint greenish-yellow, but soon with a pure yellow, color.

* Compare DIETERICH, Pharmac. Centralhalle, 1887, p. 481.

Upon cautious heating in a porcelain dish, the solution first becomes orange-red, then blue-violet, and sometimes purplish-blue streaks are formed, starting from the edge, and finally, at the temperature at which sulphuric acid begins to evaporate, an impure red-violet coloration is produced. If the heating is previously interrupted, the liquid slowly assumes in the cold a delicate cherry-red color. If the sulphuric acid contains a very minute amount of narcotin, a delicate crimson color is shown instead of the blue shades (A. HUSEMANN). The red and subsequent violet coloration of the sulphuric-acid solution also occurs, and in fact with especial delicacy, if the narcotin is dissolved in more dilute sulphuric acid (1 : 5), the colorless liquid evaporated above a small flame, and the residue then heated very cautiously (DRAGENDORFF).

6. If a very minute amount of dilute *nitric acid* is added to a cold-prepared solution of narcotin in concentrated sulphuric acid, the liquid is colored almost brown at first, but soon more and more deeply red (COUERBE). According to DRAGENDORFF, the delicacy of the reaction is heightened if the solution of narcotin in sulphuric acid is allowed to stand for one or two hours before the addition of the nitric acid. The same reaction is obtained by dissolving the narcotin in ERDMANN'S reagent (sulphuric acid containing nitric acid).* Sodium hypochlorite colors the cold-prepared, yellow sulphuric acid solution first crimson, then yellowish-red (A. HUSEMANN).

7. If a solution of narcotin in *concentrated sulphuric acid* is heated until a reddish color appears (to about 150°), and, after cooling, some *ferric chloride* is added, the portions of the liquid which are near the place where the drop of ferric chloride has entered soon become colored red with more or less of a light violet edge, but after 10 or 15 minutes a moderately permanent, cherry-red color appears (A. HUSEMANN †).

8. FRÖHDE'S reagent (sulphuric acid containing .005 g of

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* This is prepared in the following manner: Mix 6 drops of nitric acid of 1.25 sp. gr. with 100 cc of water, and allow 10 drops of this solution to flow into 20 g of pure concentrated sulphuric acid.

† Zeitschr. f. analyt. Chem., 3, 152.

sodium molybdate in 1 cc) dissolves narcotin with a green color. If the solution contains .01 g of sodium molybdate in 1 cc, the green color soon changes to a magnificent cherry-red (DRAGENDORFF).

9. *Chlorine-water* added to the solution of a narcotin salt gives a yellow color, slightly inclining to green. On the addition of ammonia, a yellowish-red and much more intense color is produced.

10. If narcotin or a salt of narcotin is dissolved in excess of dilute *sulphuric acid*, mixed with some finely powdered *manganese dioxide*, and boiled for a few minutes, the alkaloid is converted, by taking up oxygen, into opianic acid, cotarnin (a base soluble in water), and carbon dioxide. On filtering, and adding ammonia to the filtrate, no precipitate will be obtained.

11. A solution of *ammonium vanadate in concentrated sulphuric acid* (1 : 100 or 200) dissolves narcotin to a liquid which is cinnabar-red, then reddish-brown, and afterwards gradually becomes intense carmine-red (MANDELIN).

12. *Tannic acid* produces no precipitation in solutions of narcotin salts, or, at the most, only a turbidity. Upon the addition of a drop of hydrochloric acid, precipitation takes place. The precipitate dissolves upon warming, but appears again upon cooling, and it is but slightly soluble in hydrochloric acid.

13. For narcotin, the most delicate of the *general reagents for the alkaloids* are potassium mercuric iodide, iodine with potassium iodide, phosphomolybdic acid, and potassium bismuth iodide (DRAGENDORFF).*

§ 275.

2. QUININ, $C_{20}H_{24}N_2O_2$.

1. Quinin occurs in cinchona bark, accompanying cinchonin and other bases. Crystallized quinin, $C_{20}H_{24}N_2O_2$.

* In respect to other reactions for narcotin, see PALM, Zeitschr. f. analyt. Chem., 22, 226; ARNOLD, *ibid.*, 23, 230 and 233; BLOXAM, *ibid.*, 25, 247; EILOART, Chem. Centralbl., 1884, p. 850; and BROCINER, *ibid.*, 1888, p. 1294.

$3H_2O$, appears either in the form of fine crystalline needles of silky luster, which are frequently aggregated into tufts, and which effloresce readily in the air, or as a loose, white powder. Anhydrous quinin, also, may be obtained in needle-shaped crystals with a silky luster. It is sparingly soluble in cold, but somewhat more readily in hot, water. In alcohol, ether, chloroform, and carbon disulphide, it is easily or moderately soluble, while in benzol it is difficultly, and in petroleum-ether very difficultly, soluble. The taste of quinin is intensely bitter, and its solutions manifest an alkaline reaction. Crystallized quinin loses its water at 100°. It fuses at 57°, and solidifies again when it has given off its water. The anhydrous base then melts at 171.8° (HESSE).

2. Quinin neutralizes acids completely. The neutral salts taste intensely bitter. Most of them are crystallizable, difficultly soluble in cold water, but more readily soluble in hot water and in alcohol. The acid salts dissolve very freely in water. The solutions which contain an oxygen acid, especially a little sulphuric acid, in excess, opalesce with a bluish tint. If a cone of light is thrown into them, by means of a lens, either horizontally or vertically, a blue cone of light is seen even in highly dilute solutions (A. FLÜCKIGER). Aqueous solutions of quinin sulphate which are acidified with sulphuric acid rotate the ray of polarized light strongly towards the left (essential difference from cinchonin).

3. In solutions of quinin salts (if not too dilute), *potassium hydroxide*, *sodium hydroxide*, *ammonia*, as well as the *normal alkali carbonates*, produce a white, loose, pulverulent precipitate of hydrated quinin, which immediately after precipitation appears opaque and amorphous under the microscope, but assumes, after the lapse of some time, the appearance of an aggregate of crystalline needles. The precipitate redissolves only to a scarcely perceptible extent in an excess of caustic potash or soda (less easily than in water), in caustic soda less than in caustic potash (F. SESTINI), but more easily in ammonia. It is also scarcely soluble in fixed alkali carbonates. Ammonium chloride increases its solubility in water. If a solution of quinin is mixed with ammonia, ether (which contains about 2 per cent of alcohol) added, and the mixture shaken, the precipitate dissolves in the ether, and two

clear layers of liquid are formed. (In this respect, quinin differs essentially from cinchonin, which by this means may be readily detected in presence of the former, and separated from it.)

4. *Sodium bicarbonate* also produces a white precipitate, both in neutral and acid solutions of quinin salts. In acidified solutions containing 1 part of quinin to 100 parts of the liquid, the precipitate forms immediately; if the proportion of the quinin to the liquid is 1 : 150, the precipitate separates only after an hour or two, in the form of distinct needles, aggregated into groups. If the proportion is 1 : 200, the fluid remains clear, and it is only after from twelve to twenty-four hours' standing that a slight precipitate makes its appearance. The precipitate is not altogether insoluble in the precipitant, and the separation is accordingly the more complete the less the excess of the precipitant. The precipitate contains carbonic acid.

5. *Concentrated nitric acid* dissolves quinin to a colorless fluid with a bluish opalescence, turning yellowish upon application of heat.

6. The addition of strong *chlorine-water* (about $\frac{1}{8}$ volume) to the solution of a salt of quinin fails to impart a color to the fluid, or, at least, imparts to it only a very faint tint; but if ammonia is then added until it is in excess, the fluid acquires an intense emerald-green color. This characteristic reaction, the thalleiochin reaction, still occurs at a dilution of 1 : 2500. According to FLÜCKIGER, it occurs even at 1 : 4000 or 1 : 5000 if $\frac{1}{10}$ volume of chlorine-water is added without shaking, then a drop of ammonia, and after that the test-tube is gently shaken.* If, after the addition of the chlorine-water, some solution of *potassium ferrocyanide* is added, then a few drops of *ammonia* or some other alkali, the fluid acquires a magnificent deep red tint, which, however, speedily changes to a dirty brown. Upon addition of an acid (best, acetic acid) to the red fluid, the color vanishes, but reappears afterwards

* The delicacy of the reaction may be increased still more by the use of bromine instead of chlorine, but an excess, as well as a lack, of bromine prevents the appearance of the reaction more easily than an excess or a deficiency of chlorine (FLÜCKIGER, Zeitschr. f. analyt. Chem., 11, 318).

upon cautious addition of ammonia (O. LIVONIUS, A. VOGEL). Morphin prevents the thalleiochin reaction (STUART).*

7. If sulphate of quinin is dissolved in a little acetic acid, some alcohol is added, and then enough alcoholic *iodine solution* so that the liquid appears brownish-yellow, iodoquinin sulphate (herapathite) separates after a short time. This appears, according to circumstances, as a blackish-looking crystalline powder, or in the form of large crystalline plates which show a beautiful dichroism, and polarize light very powerfully (HERAPATH).† This is a very characteristic, and also, with the help of the microscope, a very delicate reaction.

8. *Concentrated sulphuric acid* dissolves pure quinin and pure quinin salts to a colorless or very faint yellowish fluid; application of a gentle heat increases the yellow color, and the application of a stronger heat turns it brown. Sulphuric acid containing an admixture of nitric acid dissolves quinin to a colorless or very faint yellowish fluid.

9. A solution of *ammonium vanadate* in *concentrated sulphuric acid* (1 : 100) is soon colored brownish-green by quinin, but after about five minutes the color becomes permanently pure green.

10. If some potassium hydroxide is fused with the addition of a drop of water, some alcoholic solution of quinin is added to the still warm mass, and it is carefully heated after the evaporation of the alcohol, the mass assumes a beautiful green color (essential difference from almost all other alkaloids, but not from quinidin). Cinchonin, cinchonidin, and cocain do not show the same color, but a similar one (W. LENZ).

11. In aqueous solutions of quinin salts, even when they are rather highly dilute, *tannic acid* produces a white precipitate. The precipitate is curdy, agglutinates on warming, and is soluble in acetic acid, also in a little hydrochloric acid; but it is thrown down again upon the addition of more hydrochloric acid.

12. The most delicate of the *general* reagents for alkaloids, in this case, are iodine with potassium iodide, potassium

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* Pharmac. Centralhalle, 1882, p. 312.

† Phil. Mag., VI, 171; Journ. f. prakt. Chem., 61, 87.

bismuth iodide, potassium mercuric iodide, picric acid, and phosphomolybdic and phosphotungstic acids (JÜRGENS).

13. In relation to the micro-chemical detection of quinin, compare SCHRAGE, Arch. f. Pharm., 1878; GODEFFROY, Zeitschr. f. allgem. Oesterr. Apothekervereins, 1878, No. 1; and BEHRENS, Chem. Centralbl., 1894, II, p. 105.

§ 276.

3. CINCHONIN, $C_{19}H_{22}N_2O$.

1. Cinchonin occurs in cinchona bark, accompanying quinin and other bases. It appears either in the form of transparent, brilliant, rhombic prisms, fine white needles, or, if precipitated from concentrated solutions, as a loose white powder. At first it is tasteless, but after some time a bitter taste of bark becomes perceptible. It is nearly insoluble in cold water, and dissolves only with extreme difficulty in hot water; it dissolves sparingly in alcohol containing water, but more readily in absolute alcohol. Hot alcohol dissolves it more abundantly than cold. From hot alcoholic solutions, the greater portion of the dissolved cinchonin separates upon cooling in a crystalline form. Solutions of cinchonin taste bitter, and manifest alkaline reaction. Cinchonin is taken up only to a slight degree by ether and by chloroform, but it dissolves with relative ease in a mixture of chloroform with $\frac{1}{4}$ to $\frac{1}{8}$ alcohol (OUDEMANS, jr.*). It is almost insoluble in petroleum-ether. In the cold, benzol dissolves amorphous cinchonin easily, but the crystalline variety with more difficulty. The latter dissolves more easily upon warming.

2. Cinchonin neutralizes acids completely. The salts have the bitter taste of bark, most of them are crystallizable, and they are generally more readily soluble in water and in alcohol than the corresponding quinin compounds. Ether and chloroform fail, or almost fail, to dissolve them. The solutions of the salts show no fluorescence, and they rotate polarized light to the right (essential difference from quinin salts).

3. Cinchonin, when heated cautiously, fuses at first without loss of water; but subsequently white fumes arise, which condense upon cold substances, like benzoic acid, in the form of

* Zeitschr. f. analyt. Chem., 12, 287.

small brilliant needles, or as a loose sublimate, a peculiar aromatic odor being exhaled at the same time. If the operation is conducted in a stream of hydrogen gas, long brilliant prisms are obtained (HLASIWETZ).

4. In solutions of cinchonin salts, *caustic potash and soda, ammonia,* and the *normal alkali carbonates* produce a white, loose precipitate of CINCHONIN, which does not redissolve in an excess of the precipitants. If the solution was concentrated, the precipitate does not exhibit a distinctly crystalline appearance, even when magnified 200 times; but if the solution was so dilute that the precipitate formed only after some time, it appears, under the microscope, to consist of distinct crystalline needles aggregated into star-shaped tufts.

5. Both from neutral and acidified solutions of cinchonin salts, *sodium* and *potassium bicarbonates* precipitate cinchonin in the same form as described in 4, but not so completely as the alkali-metal monocarbonates. Even in solutions containing 1 part of cinchonin to 200 parts of water and acid, the precipitate forms immediately; but its quantity increases after standing some time.

6. *Concentrated sulphuric acid* dissolves cinchonin to a colorless fluid, which upon application of heat first acquires a brown, and finally a black, color. Addition of some nitric acid leaves the solution colorless in the cold, but upon application of heat the fluid, after passing through the intermediate tints of yellowish-brown and brown, finally turns black.

7. If cinchonin is heated with *potassium hydroxide,* as described in the case of quinin (§ 275, 10), the projections of the solidified potassium hydroxide at first become colored reddish-brown to violet-blue, the edges being gray; afterwards the mass assumes a bluish-green color with the evolution of a somewhat pungent odor (W. LENZ).

8. A solution of *ammonium vanadate* in concentrated sulphuric acid (1 : 100) is not altered at first by cinchonin, but very gradually becomes colored permanently bluish-green.

9. The addition of *chlorine-water* to the solution of a cinchonin salt fails to impart a color to the fluid; but if ammonia is afterwards added, a yellowish-white precipitate is formed.

10. If the solution of a cinchonin salt, containing only very little or no free acid, is mixed with *potassium ferro-*

cyanide, a flocculent precipitate of CINCHONIN FERROCYANIDE is formed. If an excess of the precipitant is added, and a gentle heat very slowly applied, the precipitate dissolves, but upon cooling separates again in the form of brilliant golden-yellow scales, or in long needles, which are often aggregated in the shape of a fan. With the aid of the microscope, this reaction is as delicate as it is characteristic (CH. DOLLFUS, BILL, SELIGSOHN).

11. In aqueous solutions of cinchonin salts, *tannic acid* produces a white, flocculent precipitate, which is soluble in acetic acid, also in a small quantity of hydrochloric acid, but is reprecipitated by addition of more hydrochloric acid.

12. Those of the *general reagents* for the alkaloids which show the greatest delicacy with cinchonin are potassium mercuric iodide, iodine in potassium iodide, phosphomolybdic acid, and potassium bismuth iodide (DRAGENDORFF).

13. In regard to the micro-chemical detection of cinchonin, see BEHRENS, Chem. Centralbl., 1894, II, p. 105.

Recapitulation and Remarks.

§ 277.

Narcotin may be separated from quinin and cinchonin by repeatedly shaking the acidified solution with chloroform. If the acid liquid separated from the chloroform solution of the narcotin is made alkaline with ammonia, and is treated with ether containing about 2 per cent of alcohol, the cinchonin precipitates, while the quinin is obtained in the ethereal solution. The narcotin and the quinin are obtained by evaporating the chloroform and ether, respectively.* The alka-

* If it is a question of distinguishing quinin and cinchonin, not merely from each other, but also from the other bases occurring in cinchona bark (quinidin, cinchonidin, etc.), testing with ammonia and ether does not suffice. In relation to the methods of separating and distinguishing them, see G. KERNER, Zeitschr. f. analyt. Chem., **1**, 150, and **20**, 150; MANN, *ibid.*, **3**, 382; SCHWARZER, *ibid.*, **4**, 129; DE VRIJ, *ibid.*, **4**, 202, and **12**, 320; VAN DER BURG, *ibid.*, **4**, 273, and **9**, 179 and 305; HAGER, *ibid.*, **8**, 477, and Pharmac. Centralhalle, **21**, 411; HESSE, Zeitschr. f. analyt. Chem., **11**, 328, and **28**, 219, also Annal d. Chem., **276**, 88 and 125; GODEFFROY, Zeitschr. d. Oesterr. Apothekervereins, 1878, No. 1; GLÉNARD, Zeitschr. f. analyt. Chem., **18**, 629; C. H. WOLFF, Archiv. d. Pharmac., **219**, 1; HIELBIG, Zeitschr. f. analyt. Chem., **20**, 144, and **28**, 120; MOLNÁR, *ibid.*, **20**, 152; and ROZSNYAY, *ibid.*, **23**, 589.

loids separated in this way may be tested by the reactions described above.

THIRD GROUP.

NON-VOLATILE ALKALOIDS WHICH ARE PRECIPITATED BY POTASSIUM HYDROXIDE FROM THE SOLUTIONS OF THEIR SALTS, AND DO NOT REDISSOLVE TO ANY CONSIDERABLE EXTENT IN AN EXCESS OF THE PRECIPITANT,* BUT ARE NOT PRECIPITATED FROM (even somewhat concentrated) ACID SOLUTIONS BY THE BICARBONATES OF THE FIXED ALKALI METALS: Strychnin, brucin, veratrin, atropin.

§ 278.

1. STRYCHNIN, $C_{21}H_{22}N_2O_2$.

1. Strychnin exists in company with brucin in various kinds of *strychnos*, especially in the fruit of *S. nux vomica* and of *S. ignatii*. It appears either in the form of white, brilliant, rhombic prisms, or, when produced by precipitation or rapid evaporation, as a white powder. It gives an alkaline reaction, and has an exceedingly bitter taste. It is nearly insoluble in cold, and barely soluble in hot, water. The aqueous solution, diluted with water in the proportion of 1 : 100, still tastes noticeably bitter. Strychnin is insoluble in absolute alcohol and ether, while cold aqueous alcohol dissolves it with difficulty, but far more easily when hot. Common ether (containing some water and alcohol) dissolves a little of it. Strychnin dissolves with relative ease in acetic ether, and also in chloroform, but only to a slight degree, however, in amyl alcohol and benzol, and scarcely at all in petroleum-ether. Upon heating, it does not fuse, or scarcely does so, without decomposition. By cautious heating, it may be sublimed unchanged in small quantities (HELWIG). (Compare the foot-note on p. 674.)†

2. Strychnin neutralizes acids completely. The salts are for the most part crystallizable, and most of them are soluble in water and alcohol, but they are insoluble in ether, chloro-

* Regarding atropin, see also § 281, 4.

† According to SCHÜTZENBERGER, strychnin is not a simple body, but a complex one consisting of three alkaloids. Concerning this, compare also HAGER, Pharmac. Centralhalle, 1884, p. 181.

form, amyl alcohol, and benzol. All of them have an intolerably bitter taste, and are, like the free alkaloid, exceedingly poisonous. In concentrated aqueous solutions, the addition of small amounts of acid causes the precipitation of a part of the salt, but the precipitates redissolve upon the addition of more acid (HANRIOT and BLAREZ).

3. In solutions of strychnin salts, *potassium hydroxide*, *sodium hydroxide*, and *sodium carbonate* produce white precipitates of STRYCHNIN, which are insoluble in an excess of the precipitants. Magnified 100 times, the precipitate appears as an aggregate of small crystalline needles. From dilute solutions, the strychnin separates, only after the lapse of some time, in the form of crystalline needles, distinctly visible to the naked eye.

4. *Ammonia* produces the same precipitate as potassium hydroxide. The precipitate redissolves in an excess of ammonia; but after a short time (if the solution is highly dilute, after a considerable time), the strychnin crystallizes from the ammoniacal solution in the form of needles, which are distinctly visible to the naked eye.

5. In neutral solutions of strychnin salts, *sodium bicarbonate* produces a precipitate of strychnin, which separates in fine needles shortly after the addition of the reagent, and is insoluble in an excess of the precipitant. But upon adding one drop of acid (leaving the fluid still alkaline), the precipitate dissolves readily in the liberated carbonic acid. The addition of sodium bicarbonate to an acid solution of strychnin causes no precipitation, and it is only after the lapse of 24 hours, or even longer, that strychnin crystallizes from the fluid in distinct prisms, in proportion as the free carbonic acid escapes. If a concentrated solution of strychnin, supersaturated with sodium bicarbonate, is boiled, a precipitate forms at once; but from dilute solutions, this precipitate separates only after concentration.

6. In concentrated solutions of strychnin salts, *potassium sulphocyanide* produces immediately, but in dilute solutions after the lapse of some time, a white, crystalline prepicitate, which appears under the microscope as an aggregate of flat needles, truncated, or pointed at an acute angle, and is but slightly soluble in an excess of the precipitant.

7. In solutions of strychnin salts, *mercuric chloride* produces a white precipitate, which changes after some time to crystalline needles, aggregated into stars, and distinctly visible through a lens. Upon heating the fluid, these crystals dissolve, and upon subsequent cooling of the solution, the compound recrystallizes in larger needles.

8. If a few drops of pure *concentrated sulphuric acid* are added to a little strychnin in a porcelain dish, solution ensues, without coloration of the fluid. If small quantities of oxidizing agents (potassium chromate, permanganate, or ferricyanide, lead dioxide, or manganese dioxide) are now added (best in the solid form, as dilution is prejudicial to the reaction), the fluid acquires a magnificent blue-violet color, which, after some time, changes to wine-red, then to reddish-yellow. With potassium chromate or permanganate, the reaction is immediate. On inclining the dish, blue-violet streaks are seen to flow from the fragment of salt, and by pushing the latter about, the coloration is soon imparted to the entire fluid. With potassium ferricyanide the reaction is less rapid, but it is slowest with dioxides. The more speedy the manifestation of the reaction, the more rapid also is the change of color from one tint to another. I prefer potassium chromate, recommended by J. Otto. The reaction is especially beautiful and delicate if traces of strychnin upon a watch-glass are covered with a dilute solution of potassium dichromate. The strychnin is then gradually converted into difficultly soluble strychnin chromate. If the liquid is poured off, the residue rinsed with some water, the remainder of the liquid absorbed with blotting-paper, and the coating of strychnin chromate is brought into contact with concentrated sulphuric acid, blue or bluish-violet streaks appear at once. Strychnin chromate may also be directly precipitated from solutions of strychnin salts by means of potassium dichromate (R. Otto). Flückiger recommends a solution of .01 g of potassium dichromate in 5 cc of water which is mixed with 15 g of concentrated sulphuric acid. If a liquid containing strychnin is placed in a layer upon this solution, in a test-tube, a bluish-violet zone is obtained at the point of contact. The reaction, of course, occurs also when a trace of strychnin or a strychnin salt is

sprinkled upon the liquid mentioned above. The process is most delicate, however, when use is made of the light greenish solution (first used by GUY) of 1 part of potassium permanganate in 2000 parts of concentrated sulphuric acid. WENZELL * states that he has succeeded in distinctly detecting .0005 mg of strychnin, by the aid of this solution. Since, with solutions of potassium permanganate in sulphuric acid, other organic substances also yield colorations which are similar to that produced by strychnin, it is not advisable to make use of potassium permanganate when the substance to be tested for strychnin contains other organic matters. In this case, potassium dichromate is to be preferred (SEDGWICK†). Chlorides and somewhat large amounts of nitrates, as well as considerable amounts of other organic substances, interfere with or prevent the reaction. It is therefore advisable first to separate the strychnin as far as possible from other substances before applying the decisive reaction. If the red solution (colored by manganese dioxide) is mixed with from 4 to 6 times its volume of water, heating being avoided, and ammonia is then added until the reaction is *nearly* neutral, the fluid shows a magnificent violet-purple tint; upon the addition of more ammonia, the color becomes yellowish-green to yellow (J. ERDMANN). I have found, however, that this reaction is seen only where larger, though still very minute, quantities of strychnin are present. Morphin, when present at the same time, interferes with or prevents these strychnin reactions.‡ In order to produce the strychnin reaction with certainty in the presence of morphin, the concentrated, aqueous, neutral solution of the salts is mixed with potassium ferricyanide (NEUBAUER) or normal potassium chromate (HORSLEY), and filtered. The precipitate contains the strychnin as ferricyanide or chromate, respectively, while the solution contains the soluble morphin salts. In either case, the precipitate is washed a little, dried, and mixed in a watch-glass with strong sulphuric acid, when the blue-violet color is immediately produced. It

* Pharmac. Centralhalle, 1871, p. 234.

† Zeitschr. f. analyt. Chem., 20. 421.

‡ REESE. Zeitschr. f. analyt. Chem., 1, 399; and HORSLEY, *ibid.*, 1, 515. (Compare, on the other hand, THOMAS, *ibid.*, 1, 417.)

like the free alkaloid, are poisonous. Most of them are crystallizable.

3. From solutions of brucin salts, *potassium hydroxide*, *sodium hydroxide*, and *sodium carbonate* throw down a white precipitate of brucin, insoluble in an excess of the precipitant. Viewed under the microscope, immediately after precipitation, this appears to consist of very minute grains; but upon further inspection, these grains are seen (with absorption of water) to change suddenly into needles, which subsequently arrange themselves, without exception, into concentric groups. These successive changes of the precipitate may be distinctly traced, even with the naked eye.

4. In solutions of brucin salts, *ammonia* produces a whitish precipitate, which appears at first like a number of minute drops of oil, but subsequently changes (with absorption of water) to small needles. Immediately after separation, the precipitate redissolves very readily in an excess of the precipitant; but after a very short time (in dilute solutions, after a longer time), the brucin, combined with water, crystallizes from the ammoniacal fluid in small, concentrically grouped needles, which the further addition of ammonia fails to redissolve.

5. In neutral solutions of brucin salts, *sodium bicarbonate* produces a precipitate of brucin, combined with water. This precipitate separates, after a short time, in the form of concentrically aggregated needles of silky luster, which are insoluble in an excess of the precipitant, but dissolve in free carbonic acid (compare strychnin). Sodium bicarbonate fails to precipitate acid solutions of brucin salts; and it is only after a considerable time, and with the escape of the carbonic acid, that the hydrated alkaloid separates from the fluid in comparatively large crystals.

6. *Concentrated nitric acid* dissolves brucin and its salts to intensely red fluids, which immediately acquire a yellowish-red tint, and turn yellow upon the application of heat. Upon the addition of stannous chloride or colorless ammonium sulphide to the fluid, heated to this point, either while concentrated or after dilution with water, the faint yellow tint changes to a most intense violet. From concentrated solutions, there separates also a violet precipitate. If hydrogen sodium sul-

phide is used, instead of the reducing agents mentioned, the violet color, first appearing, afterwards changes to green (ST. COTTON *).

7. If a little brucin is treated with a few drops of pure *concentrated sulphuric acid*, a solution of a faint rose-color is obtained, which afterwards turns yellow. If a small amount of sulphuric acid containing *nitric acid* (ERDMANN'S acid mixture †) is added, the fluid transiently acquires a red, afterwards a yellow, color. The reaction is very delicate.

8. If a solution of a brucin salt is mixed with a solution of *mercurous nitrate* which contains as little free acid as possible, a colorless liquid results. If the mixture is now placed upon a moderately heated water-bath a beautiful carmine color gradually appears, which slowly increases in intensity and is very stable. Strychnin produces no reddening. One part of brucin in 10 or 20 parts of strychnin may be distinctly recognized in this manner (FLÜCKIGER ‡).

9. If brucin is brought into a solution of *ammonium vanadate* in *concentrated sulphuric acid* (1 : 200), the solution transiently becomes yellowish-red, then reddish-orange, but soon loses its color (MANDELIN §).

10. If the solution of a brucin salt is mixed with potassium dichromate, it remains clear at first, but after some time yellowish-red crystals separate, which dissolve in concentrated sulphuric acid with a brownish-red color.

11. Careful addition of *chlorine-water* to the solution of a salt of brucin imparts to the fluid a fine bright red tint, and if ammonia is then added, the red color changes to yellowish-brown. If solid brucin is covered with a little chlorine-water, it dissolves to a light red liquid which becomes colorless upon the addition of more chlorine-water, the latter yielding a blood-red residue upon being evaporated to dryness upon the water-bath (BECKURTS). (Essential difference from strychnin.)

12. *Potassium sulphocyanide* produces in concentrated solutions of salts of brucin immediately, in dilute solutions after some time (especially upon rubbing the surface of the glass

* Zeitschr. f. analyt. Chem., 9, 111.

† For its preparation, see foot-note, p. 684.

‡ Zeitschr. f. analyt. Chem., 15, 342.

§ Zeitschr. f. analyt. Chem., 23, 236.

under the liquid), a granular, crystalline precipitate, which, under the microscope, appears composed of variously aggregated, polyhedral, crystalline grains.

13. If brucin is dissolved in acetic acid, some water is added, and then a little *lead dioxide*, a rose-red coloration of the liquid is produced (IHL).

14. *Mercuric chloride* produces a white, granular precipitate, which, under the microscope, appears composed of small, roundish, crystalline grains.

15. In solutions of salts of brucin, *tannic acid* produces heavy, dirty-white precipitates, soluble in acetic acid, but insoluble in hydrochloric acid.

16. The most delicate of the *general reagents* for brucin are iodine in potassium iodide, potassium mercuric iodide, phosphomolybdic acid, and potassium bismuth iodide.*

§ 280.

3. VERATRIN.†

1. Veratrin occurs in various species of veratrum, especially in the seeds of *Veratrum sabadilla*, and in small amount in the root of *Veratrum album* and of *Veratrum lobelianum*. It appears as a white, loose, odorless powder of acrid and burning, but not bitter, taste, and is exceedingly poisonous. Its dust, when entering the nose in the minutest quantity,

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* Concerning other reactions for brucin, see HAGER, Zeitschr. f. analyt. Chem., 11, 201; BUCKINGHAM, *ibid.*, 13, 235; DRAGENDORFF, *ibid.*, 18, 108; FRAUDE, *ibid.*, 19, 87; PALM, *ibid.*, 22, 226; ARNOLD, *ibid*, 23, 229 and 232.

† The officinal veratrin, which is usually understood by the name "veratrin," is an intimate mixture of two isomeric alkaloids. They have the formula, $C_{32}H_{49}NO_9$. One of the alkaloids, crystallized veratrin or cevadin, is crystallizable and almost insoluble in water. The other, veratridin, is not crystallizable and is soluble in water. But the two do not admit of separation by means of water, since a small amount of cevadin makes the veratridin insoluble in water, while, on the other hand, a small amount of veratridin deprives the cevadin of its power of crystallizing (BOSETTI). The statements given in the text refer to the officinal veratrin. In relation to separating the mixed alkaloids, see E. SCHMIDT and R. KÖPPEN, Annal. d. Chem., 185, 224, and BOSETTI, Zeitschr. f. analyt. Chem., 25, 249.

excites the most violent sneezing. Veratrin dissolves in water only in very slight amount, but to a greater extent when freshly precipitated than after drying. The solution has a burning taste, and reacts faintly alkaline. The cold saturated solution becomes turbid upon heating, but becomes clear again upon cooling if the heating has not been continued for a long time. Veratrin dissolves in 2 parts of chloroform, in 3 parts of alcohol, somewhat less in ether, amyl alcohol, and benzol, and is still less soluble in petroleum-ether. At 150°, it fuses like wax, and upon cooling, changes into a yellow, translucent mass. Upon cautious heating, it may be sublimed unchanged (compare the foot-note on p. 674).

2. Veratrin neutralizes acids completely. Some veratrin salts are crystallizable with difficulty, but most of them dry up to a gummy mass, while some are soluble in water, and have an acrid and burning taste.

3. In solutions of veratrin salts, *potassium hydroxide, sodium hydroxide, ammonia,* and the *alkali monocarbonates* produce a flocculent white precipitate, which, when viewed under the microscope immediately after precipitation, does not appear crystalline. After the lapse of a few minutes, however, it alters its appearance, and, instead of the original coagulated flakes, small scattered clusters of short prismatic crystals are observed. The precipitate does not redissolve in an excess of potassium or sodium hydroxide or of potassium carbonate. It is slightly soluble in ammonia in the cold, but the dissolved portion partially separates again upon application of heat.

4. With *sodium bicarbonate* and *potassium bicarbonate,* the salts of veratrin comport themselves like those of strychnin and brucin. However, upon boiling, the veratrin separates readily, even from dilute solutions.

5. If veratrin is acted upon by *concentrated nitric acid,* it agglutinates into small resinous lumps, which dissolve slowly in the acid. If the veratrin is pure, the solution is colorless. If the solution is evaporated to dryness on the water-bath, and the residue moistened with concentrated alcoholic potash, it becomes dark brown, or often dark reddish-brown, and evolves a strong odor resembling that of coniin.

6. If veratrin is treated with *concentrated sulphuric acid,* it also agglutinates at first into resinous lumps; but these dis-

solve with readiness to a faint yellow fluid, having a greenish-yellow fluorescence at first. The yellow color, however, gradually increases in depth and intensity, and changes afterwards to a reddish-yellow, then to an intense blood-red, and finally to purple-red. The color persists 2 or 3 hours, then gradually disappears. Upon warming, the red color appears at once. Cubebin gives a similar reaction (SCHÄR).

7. If a little pulverized *sugar* is sprinkled upon the yellow solution of veratrin in concentrated sulphuric acid, spread out in a thin layer, there soon occurs, from the absorption of moisture, a dark green color, which slowly becomes intensely blue, and then gradually fades (WEPPEN*). The appearance of the green coloration is hastened by breathing upon the acid. This reaction also occurs very beautifully, if 1 part of veratrin is triturated with 6 parts of sugar (BECKURTS), not much more nor much less (R. OTTO), and the whole is then mixed with not too much sulphuric acid.

8. A solution of *ammonium vanadate in concentrated sulphuric acid* (1 : 100) is colored by veratrin first brownish-red, and afterwards dark reddish-violet (KUNDRÁT).

9. If veratrin is dissolved in *strong hydrochloric acid*, a colorless fluid is obtained, which by long boiling gradually acquires a reddish, and finally an intensely red, tint, which is permanent on standing. The reaction is very delicate (TRAPP).

10. *Potassium sulphocyanide* produces flocculent, gelatinous precipitates, only in concentrated solutions of veratrin salts.

11. Addition of not too little *chlorine-water* to the solution of a veratrin salt imparts to the fluid an intense yellow color, which is not essentially changed upon the addition of ammonia.

12. For veratrin, the most delicate of the *general reagents* for the alkaloids are phosphomolybdic acid, iodine with potassium iodide, potassium mercuric iodide, and tannic acid.†

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* Zeitschr. f. analyt. Chem., 13, 454.

† In relation to further reactions for veratrin, see BUCKINGHAM, Zeitschr. f. analyt. Chem., 13, 235; GODEFFROY, *ibid.*, 15, 244; JORISSEN, *ibid.*, 19, 359; ROSSBACH, action upon infusoria, *ibid.*, 21, 482; ARNOLD, *ibid.*, 23, 231 and 234.

§ 281.

4. Atropin, $C_{17}H_{23}NO_3$.

1. Atropin occurs in all parts of the deadly nightshade (*Atropa belladonna*) and of the thorn-apple (*Datura stramonium*), together with hyoscyamin (Ladenburg, E. Schmidt).* It forms small, brilliant prisms and needles. When pure, it is without odor, and is nauseously and persistently bitter to the taste. It fuses at 115° to 116° to a colorless liquid, which solidifies in a crystalline condition upon cooling. It volatilizes at 140°, with partial decomposition. Atropin dissolves with difficulty in cold, somewhat more easily in boiling, water. The solution gives an alkaline reaction, and, upon boiling, some of the atropin volatilizes with the steam. Animal charcoal takes it up from its aqueous solution. Atropin dissolves easily in alcohol, and the solution is optically inactive (Poehl). It dissolves very easily in chloroform and in amyl alcohol, but more difficultly in ether and in benzol, and scarcely at all in petroleum-ether.

2. Atropin combines with acids, forming salts, some of which, particularly the acid salts, do not crystallize, or do so only with difficulty. The salts dissolve easily in water and alcohol, but are nearly or quite insoluble in ether, benzol, and amyl alcohol. The aqueous solutions of the salts acquire a dark color by long heating.

3. Atropin and its salts are active narcotic poisons. When applied to the eye, they dilate the pupil for a considerable time. (Hyoscyamin has the same action; but the dilation in this case is rather slower in making its appearance, and more lasting. Cocain also dilates the pupil, but only upon the use of a somewhat more concentrated solution.)

4. *Potassium hydroxide, sodium hydroxide,* and *fixed alkali monocarbonates,* added to concentrated aqueous solutions of atropin salts, precipitate a portion of the alkaloid. The pre-

* E. Schmidt and H. Henschke (Chem. Centralbl., 1888, p. 549) also found atropin with hyoscyamin and hyoscin in the root of *Scopolia japonica.* In regard to the other alkaloids occurring with atropin and hyoscyamin in belladonna, and their properties, compare O. Hesse, Annal. d. Chem., **261**, 87, and **271**, 100.

cipitate, which is at first pulverulent, does not dissolve in excess of the precipitant more readily than in water. By long standing, it becomes crystalline. *Ammonia* likewise produces a precipitate, soluble in an excess. Atropin is decomposed in contact with fixed alkalies or with baryta-water, slowly in the cold, rapidly on heating, with the formation of atropic acid and tropin.

5. *Ammonium carbonate* and *alkali bicarbonates* do not produce precipitates in solutions of atropin salts.

6. *Hydrochlorauric acid*, added to aqueous solutions of atropin salts, throws down atropin hydrochlorauride in the form of a yellow precipitate, which gradually becomes crystalline. The compound forms small plates, devoid of luster, which fuse at 135° to 137° (LADENBURG).

7. In aqueous solutions of salts of atropin, *tannic acid* produces a white, curdy precipitate, soluble in ammonia and in hydrochloric acid.

8. If atropin is warmed with *concentrated sulphuric acid* to slight browning, and a little water is added, an agreeable odor is evolved during the frothing, recalling that of the sloe blossom (GULIELMO). If a fragment of potassium dichromate is added to the hot mixture, the odor which now escapes recalls that of the blossoms of *Spiræa ulmaria*. If the warming is continued, it is similar to that of bitter-almond water (PFEIFFER). The odor of flowers characteristic of atropin may be also produced by bringing some atropin upon a few chromic-acid crystals, and heating gently until the chromic acid assumes a green color in consequence of the commencement of reduction (BRUNNER).

9. If atropin or an atropin salt is covered with a little *fuming nitric acid*, and the mixture is evaporated to dryness upon the water-bath, a colorless residue is obtained. If, after cooling, a drop of a solution of *potassium hydroxide* in absolute alcohol is added, a violet coloration results, which soon changes into red (VITALI). Strychnin and many ptomains behave similarly (MENEGAZZI, CIOTTO, and SPICA). Concerning the *different* behavior of atropin and strychnin in this reaction, compare, however, VITALI, Chem. Centralbl., 1894, II, p. 816.

10. If atropin, together with *concentrated sulphuric acid*, is

placed upon a white porcelain surface, and a few crystals of *potassium nitrite* are stirred into the mixture, the latter assumes a deep yellow to orange color. If a few drops of a solution of potassium hydroxide in alcohol are now added, the mixture becomes magnificently red-violet, and then soon pale pink (ARNOLD).

11. In an alcoholic solution of atropin, an aqueous solution of *mercuric chloride* produces at once a yellowish precipitate, which becomes orange-red upon gentle warming (GERRARD).

12. *Picric acid* acts in various ways upon the atropins occurring in commerce. In a solution of the English atropin sulphate, a turbidity is produced which is caused by amorphous globules. After warming until the turbidity dissolves, and then cooling, beautiful rectangular crystalline plates are formed. The German atropin sulphate, on the other hand, gives at once, with picric acid, an essentially crystalline precipitate, and an amorphous turbidity only to a small extent. These crystals are also rectangular plates (HAGER).*

13. For atropin, the most delicate of the *general reagents* for the alkaloids are iodine in potassium iodide, and phosphoantimonic acid.†

Recapitulation and Remarks.

§ 282.

Strychnin may be separated from brucin, veratrin, and atropin, by means of cold absolute alcohol, since it is insoluble in that liquid, while the latter alkaloids readily dissolve in it. Strychnin may also be separated from brucin by means of potassium chromate. For this purpose, the alkaloids are brought into as concentrated a solution as possible, faintly acidified with acetic acid, and potassium chromate is

* According to POEHL, picric acid acts indifferently towards pure atropin salts (Zeitschr. f. analyt. Chem., 18, 629).

† In relation to further reactions for atropin, see GODEFFROY, Zeitschr. f. analyt. Chem., 16, 244; ROSSBACH, action upon infusoria, *ibid.*, 21, 482; VITALI, *ibid.*, 21, 581; PALM, *ibid.*, 22, 226; FLÜCKIGER, Chem. Centralbl., 1886, p. 504.

added. Almost all the strychnin then separates as chromate, while the brucin remains dissolved (R. OTTO). By means of chlorine-water, also, the two alkaloids may be easily recognized in the presence of each other and separated, for if they are treated with it in the dry state, the brucin dissolves to a red liquid (§ 279, 11), while the strychnin remains behind (BECKURTS). Strychnin may be identified best by the reaction with sulphuric acid and the oxidizing agents mentioned in § 278, 8;* also by its crystalline form observed under the microscope, when it has been precipitated with alkalies; or finally by the form of the precipitate produced by potassium sulphocyanide or mercuric chloride. Brucin and veratrin may be separated from atropin by shaking the alkaline solution with petroleum-ether (DRAGENDORFF). The latter takes up the brucin and veratrin, but not the atropin. By separating the aqueous fluid from the petroleum-ether, and shaking it with ether, the atropin may be obtained in ethereal solution. Brucin and veratrin are not readily separated from each other, but may be detected in presence of each other. The identity of brucin is best established by the reactions with nitric acid and stannous chloride or ammonium sulphide, or by the form of the crystalline precipitate which ammonia produces in solutions of salts of brucin. Veratrin is sufficiently distinguished from brucin and the other alkaloids considered here, by its characteristic deportment when heated, and also by the form of the precipitate which alkalies produce in solutions of its salts. To detect veratrin in presence of brucin, the reaction with concentrated sulphuric acid or with hydrochloric acid is selected.

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* Besides curarin (see above), the only other body which acts somewhat similarly in this respect is anilin. A. GUY, however, has called attention to the fact that anilin, when treated with sulphuric acid and oxidizing agents, first assumes a pale green color, which gradually becomes darker, and only after that takes on a magnificent blue color, which persists for a long time, and finally changes to black. Brucin essentially disturbs the color-reaction with sulphuric acid and potassium dichromate. The reaction is, however, still distinct upon using 1 mg of strychnin to 20 mg of brucin, but it is indistinct with 1 mg to 40 mg (BECKURTS).

C. Properties and Reactions of certain non-nitrogenous Bodies allied to the Alkaloids.

In connection with the alkaloids, salicin, digitalin, and picrotoxin will be considered, although they do not belong to the same class of chemical compounds.

§ 283.

1. Salicin, $C_{13}H_{18}O_7$.

1. Salicin exists in the bark and leaves of most kinds of willow and some kinds of poplar. It appears either in the form of white crystalline needles and scales of silky luster, or, where the crystals are very small, as a powder of silky luster. It has a bitter taste, and dissolves somewhat difficultly in cold water and cold alcohol, but readily at the boiling temperature. It is insoluble in ether, but soluble in caustic potash solution as well as in glacial acetic acid. It fuses at 198°, and decomposes at a higher temperature.

2. Salicin is precipitated by almost no reagent in such a way that it is present as such in the precipitate, but, from concentrated, hot aqueous solutions, *lead acetate* precipitates a white compound of SALICIN and LEAD OXIDE.

3. If salicin is brought into *concentrated sulphuric acid*, it agglutinates into a resinous lump, and acquires an intensely blood-red color, without dissolving; while the color of the sulphuric acid is at first unaltered. Solution takes place only slowly, and, to the extent that this is effected, the acid also becomes red.

4. If an aqueous solution of salicin is mixed with *dilute sulphuric acid* or with *hydrochloric acid*, and boiled for a short time, it suddenly becomes turbid, grape-sugar being formed, and deposits a white agglutinating precipitate (SALIRETIN). If the liquid containing the precipitate is now mixed with 1 or 2 drops of potassium chromate and boiled, the saliretin acquires a bright rose color, the characteristic odor of salicylic aldehyde being emitted at the same time. If the boiling with dilute sulphuric acid and potassium chromate is con-

ducted in a small distilling apparatus, the receiver of which contains a little water, the salicylic aldehyde in its contents may be easily detected by adding a drop of neutral ferric chloride solution, which produces an intense violet coloration (PARROT.)

5. *Ferric chloride* colors solutions of salicin slightly brownish, and upon boiling, the liquid is decolorized, with the formation of an ochre-yellow precipitate.

6. If salicin is brought into a solution of *silver nitrate* containing an excess of ammonia and some potassium or sodium hydroxide, and heat is applied, a fine mirror of silver is formed from reduction. Other glucosides, mannite, and cane-sugar, as well as grape-sugar, yield the same reaction (E. SALKOWSKI).

7. If a little salicin is moistened with a few drops of a solution of *zinc chloride* in dilute hydrochloric acid (.1 g of fused zinc chloride, 3 cc of fuming hydrochloric acid, 3 cc of water), and it is allowed to become dry on the water-bath, an intense violet-red residue is obtained (A. JORISSEN).

8. Salicin does not saturate acids, nor does it combine with them.

§ 284.

2. DIGITALIN.*

1. The preparations occurring in commerce under the name digitalin vary greatly in their properties. They consist of mixtures of the active principles of *Digitalis purpurea* and their decomposition products. SCHMIEDEBERG mentions the following: DIGITOXIN (very poisonous), DIGITALIN, in a restricted sense, and DIGITALEIN (both poisonous), and DIGITONIN (slightly active).† Other investigators have arrived at different results, so that the investigation of the active constituents of digitalis cannot yet be considered as finished. The constituents are present in the digitalin of commerce in

* In regard to the formula of digitalin, compare ARNAUD, Chem. Centralbl., 1889, II, p. 1049.

† N. Rep. Pharm., 24, 89; Chem. Centralbl., 1875, p. 262, where the properties of the separate substances are given.

widely varying proportions. They are nitrogen-free, and belong to the glucosides or to the bitter principles.

2. For practical purposes, two kinds of commercial digitalin are to be especially considered, viz., the GERMAN, soluble in water, and the FRENCH, but slightly soluble in water, both of which show similar physiological action. According to most of the statements, German digitalin is amorphous, but according to R. OTTO, it is a powder which appears crystalline under the microscope. It dissolves in cold water to a neutral, turbid, bitter liquid, which froths abundantly upon shaking. Alcohol and amyl alcohol dissolve it completely, ether, benzol, and chloroform partly, and petroleum-ether not at all. The French digitalin (NATIVELLE'S) occurs in fine, loose needles, united in bundles, possessing a neutral reaction. It yields a bitter taste only slowly, scarcely dissolves in water, does not dissolve in ether or benzol, but dissolves easily in chloroform and in alcohol. The French digitalin of HOMOLLE shows somewhat varying properties. It forms a white or yellowish-white, warty or scaly mass of neutral reaction and very bitter taste, which dissolves very slightly in water, easily in 90 per cent alcohol, but difficultly in ether. After moistening with glacial acetic acid, all kinds of digitalin dissolve upon addition of water (DRAGENDORFF *).

3. If a solution of commercial digitalin, prepared by the aid of glacial acetic acid, is shaken with *chloroform* at 35°, the active constituents of it, or at least the greater part of them, are obtained in the chloroform. They remain behind after washing the chloroform with water, filtering,† and allowing it to evaporate at about 30°.

4. If commercial digitalin, or the residue obtained in 3 by the evaporation of the chloroform extract, is treated with *concentrated sulphuric acid*, or even with sulphuric acid containing one or two molecules of water for each molecule of sulphuric acid (which is to be preferred in the presence of foreign organic substances, DRAGENDORFF), and one or two drops of

* "Gerichtlich-chem. Ermittelung von Giften." 3te Aufl. (Vandenhoeck und Ruprecht, Göttingen), 1888, p. 304. In regard to the action of various kinds of digitalin, compare G. BARDET, Chem. Centralbl., 1890, I, p. 407.

† If the chloroform solution appears mucilaginous, a few drops of absolute alcohol should be added before filtering.

bromine solution are added by means of a glass rod, there appears, upon stirring, a characteristic,* more or less pure, purple coloration.† For the bromine solution, DRAGENDORFF recommends a solution of 1 part of potassium hydroxide in 5 parts of water, to which just enough bromine is added to color it permanently yellow. This reaction, which was first proposed by GRANDEAU and by J. OTTO (who used bromine-water), and which has been confirmed by DRAGENDORFF and others, is very delicate, and takes place very distinctly, according to the experiments of the latter, even with .0002 g of commercial digitalin.

5. A solution of *ammonium vanadate* in *concentrated sulphuric acid* (1:100) is colored by digitalin intensely dark brown, with a red tint, afterwards very dark brown (KUNDRÁT).

6. Freshly precipitated *lead hydroxide* extracts all the digitalin from its aqueous as well as alcoholic solutions, upon long shaking therewith. The filtered compound, pressed between blotting-papers, when treated with concentrated sulphuric acid, becomes flesh-colored or light fawn-colored. Bromine changes the color, after long standing, to emerald-green (PALM).

7. In addition to the reaction mentioned in 4, special attention should be paid in chemico-legal investigations to the *physiological action* of the residue obtained, according to 3, by the evaporation of the chloroform extract (DRAGENDORFF ‡).

§ 285.

3. PICROTOXIN, $C_{30}H_{34}O_{13}$.

1. Picrotoxin is the poisonous principle of the fruit of *Menispermum cocculus*, L. It forms colorless needles, usually

* DELPHININ shows a similar behavior, but this, upon shaking an acid solution with chloroform, does not pass into the latter, or at least not more than traces of it thus dissolve.

† CUBEBIN yields a similar reaction (SCHÄR). FLUCKIGER observed a differing deportment in the case of NATIVELLE'S crystallized digitalin (Pharmac. Centralhalle, 1873, p. 275).

‡ "Beiträge zur gerichtlichen Chemie einzelner organischer Gifte" (H. Schmitzdorff, St Petersburg), 1872, p. 34. In regard to further reactions for digitalin, compare BROCINER, Chem. Centralbl., 1890, I, p. 1079; BRUNNER, "Gerichtl.-chem. Ermittelung von Giften," von DRAGENDORFF, Göttingen 1888, p. 137; LAFON, Zeitschr. f. analyt. Chem., 25, 567.

grouped in star-shaped forms. It is without odor, reacts neutral, tastes very bitter, is a narcotic poison, fuses at 199° to 200°, yielding empyreumatic fumes.

2. Picrotoxin dissolves with some difficulty in cold, but more easily in boiling, water, and on cooling and evaporation crystallizes from the solution in needles. Hot alcohol dissolves it with extreme facility. When cold, the concentrated solution solidifies to a silky mass; while more dilute solutions give silky needles when evaporated. Picrotoxin is difficultly soluble in ether and chloroform, but is easily soluble in amyl alcohol and in glacial acetic acid. Upon shaking its acid solution with ether, chloroform, or amyl alcohol (not, however, with benzol or petroleum-ether), the picrotoxin goes into these solvents. Upon shaking its alkaline solutions, on the other hand, it is not taken up, or only in traces, by ether, chloroform, or amyl alcohol. The ethereal solution, when evaporated, leaves the picrotoxin in the form of powder or scaly crystals. Upon long treatment with very much benzol in the cold, picrotoxin splits into picrotoxinin and picrotin (E. SCHMIDT *).

3. *Acids* do not neutralize picrotoxin, and, with the exception of acetic acid, do not increase its solubility in water.

4. *Ammonia*, *potassium hydroxide*, and *sodium hydroxide* solutions dissolve picrotoxin freely. Acids, even carbonic acid, precipitate it from the concentrated solutions. Picrotoxin therefore possesses the character of an acid rather than of a base. When heated, the solutions of picrotoxin in caustic potash or soda acquire a yellow or yellowish-red color.

5. If picrotoxin is brought together with *concentrated sulphuric acid*, it dissolves with a saffron-yellow color, and, if a trace of *potassium dichromate* is now added, a violet-red coloration is produced, which changes finally to apple-green (KÖHLER).

6. If dry commercial picrotoxin is triturated with three times its amount of *potassium nitrate*, the mixture is moistened with *sulphuric acid*, and then a very strong solution of sodium hydroxide is put upon it in excess, the mass and the resulting

* Compare, however, in this connection, the articles of v. BARTH and KRETSCHY, Zeitschr. f. analyt. Chem., 19, 360, and 21, 582, and Monatshefte f. Chem., 5, 65.

solution show a brick-red color. The color slowly disappears (LANGLEY). DRAGENDORFF has modified the reaction in the following manner: Moisten the picrotoxin with a little concentrated *nitric acid*, warm upon the water-bath until the residue has become dry, moisten it with as little concentrated *sulphuric acid* as possible, and then cover it with an excess of strong sodium hydroxide. A faint red coloration was thus produced with even .1 mg.

7. If a picrotoxin solution containing some sodium or potassium hydroxide is mixed with a solution of *potassium cupric tartrate* (FEHLING'S solution) and it is gently warmed, cuprous oxide separates out.

8. A solution of *ammonium vanadate in concentrated sulphuric acid* (1 : 100) is colored faintly brown by picrotoxin. The color gradually becomes darker, and, after a considerable time, dark green.

9. When shaken for a long time with the aqueous as well as the alcoholic solution of picrotoxin, freshly precipitated lead hydroxide extracts the whole of it from the solution. The compound, filtered and pressed between blotting-papers, when treated with concentrated sulphuric acid, first becomes yellow, upon longer standing yellowish-red, and after very moderate heating violet-red (PALM).

10. *Iodine in potassium iodide, picric acid, tannic acid, gold chloride*, and *platinic chloride* do not cause precipitation in picrotoxin solutions.*

D. SYSTEMATIC COURSE FOR THE DETECTION OF THE ALKALOIDS UNDER CONSIDERATION, AND OF SALICIN, DIGITALIN, AND PICROTOXIN.

In the following courses of analysis, described under *a* and *b*, it is presupposed that one or several of the *non-volatile* alkaloids, etc., are in concentrated solution, dissolved in water by the agency of acids, and free from any other substances which would obscure or modify the reactions. When we have become acquainted with the course to be followed

* In relation to the detection of picrotoxin by means of physiological experiments, compare DRAGENDORFF, "Beiträge zur gerichtl. Chem.," Wienecke, St. Petersburg, 1884, p. 49.

under these conditions, the most advisable methods to be used in obviating the interfering influence of coloring or extractive matters, etc., will be described under *c*, and then the detection of *volatile* alkaloids will be also taken into consideration.

a. DETECTION OF THE NON-VOLATILE ALKALOIDS, ETC., IN SOLUTIONS ASSUMED TO CONTAIN ONLY ONE OF THESE SUBSTANCES.

§ 286.

1. To a portion of the solution, add a drop of dilute sulphuric acid and then some solution of iodine in potassium iodide or of phosphomolybdic acid.

a. NO PRECIPITATE IS FORMED: absence of all alkaloids; possible presence of salicin, digitalin, or picrotoxin. Pass on to 5.

b. A PRECIPITATE IS FORMED. There is cause to suspect the presence of an alkaloid. Pass on to 2.

2. To a portion of the aqueous solution, add dilute potassium or sodium hydroxide solution drop by drop, till the fluid acquires a scarcely perceptible alkaline reaction, stir, and allow it to stand for some time.

a. NO PRECIPITATE IS FORMED. If the solution was concentrated, this is a positive indication of the absence of all alkaloids; but if the solution was somewhat dilute, there is a possibility that atropin may be present. After previous evaporation, therefore, test further portions of the solution, if necessary, according to § 281, 6, 8, and 9, with hydrochlorauric acid, by heating with sulphuric acid and by treating with concentrated nitric acid, etc., for ATROPIN.

b. A PRECIPITATE IS FORMED. Add potassium or sodium hydroxide solution drop by drop till the fluid is strongly alkaline, and if it does not become clear even after long standing, add some more water.

α. THE PRECIPITATE DISAPPEARS: morphin, cocain, or atropin. Test a fresh portion of the solution with iodic acid (§ 271, 13).

aa. Separation of iodine: MORPHIN. Confirm by § 271, 7, 8, and 9.

bb. No separation of iodine: COCAIN or ATROPIN. Test for the former with potassium chromate in weak hydrochloric acid solution (§ 272, 9), and for atropin as in *a*.

β. THE PRECIPITATE DOES NOT DISAPPEAR: presence of an alkaloid of the second or third group (atropin excepted). Pass on to 3.

3. To another portion of the original solution, add two or three drops of dilute sulphuric acid, then a saturated solution of sodium bicarbonate, till the acid reaction just vanishes; stir actively with a glass rod, rubbing the sides of the vessel, and allow the fluid to stand half an hour.

a. NO PRECIPITATE IS FORMED: absence of narcotin and cinchonin. Pass on to 4.

b. A PRECIPITATE IS FORMED: narcotin, cinchonin, perhaps also quinin (since its precipitation by sodium bicarbonate is entirely dependent on the amount of water present). To a portion of the original solution, add ammonia in excess, then ether containing about 2 per cent of alcohol (in not too small amount), and shake.

α. THE PRECIPITATE REDISSOLVES IN THE ETHER, THE FLUID PRESENTING TWO CLEAR LAYERS: narcotin or quinin. To distinguish between them, test a fresh portion of the original solution with chlorine-water and ammonia. If the solution turns green, QUININ, if yellowish-red, NARCOTIN, is present. To confirm for narcotin apply the test with sulphuric acid containing nitric acid (§ 274, 6).

β. THE PRECIPITATE DOES NOT REDISSOLVE IN THE ETHER: CINCHONIN. To confirm, test the deportment on heating (§ 276, 3), or with potassium ferrocyanide (§ 276, 10).

4. Put a portion of the original dry substance, or of the residue obtained by evaporating the original solution, in a watch-glass, and add concentrated sulphuric acid.

a. A faint rose-colored solution is obtained, which becomes intensely red upon addition of nitric acid: BRUCIN. Confirm by nitric acid and stannous chloride (§ 279, 6).

b. A yellow solution is obtained, which gradually turns yellowish-red, blood-red, and purplish-red: VERATRIN.

c. A colorless solution is obtained, which remains colorless on standing. Add a fragment of potassium chromate; a deep blue coloration indicates STRYCHNIN, while no change indicates QUININ. Confirm by chlorine-water and ammonia.

5. To determine whether salicin, digitalin, or picrotoxin is present, mix a portion of the original dry substance, or the dry residue obtained by evaporation, with concentrated sulphuric acid.

a. The substance becomes colored blood-red at once, and slow solution takes place, with the formation of a red liquid: SALICIN. Confirm by heating a portion of the solution with dilute sulphuric acid or with hydrochloric acid (§ 283, 4).

b. The substance dissolves with a saffron-yellow color, and upon the addition of a trace of potassium dichromate, a violet-red, and finally an apple-green, coloration results: PICROTOXIN. Confirm with nitric acid and sodium hydroxide solution (§ 285, 6).

c. The sample dissolves with a reddish-brown color, which, upon the addition of a drop of bromine solution, changes into a more or less pure purple color (§ 284, 4): DIGITALIN.

b. DETECTION OF THE NON-VOLATILE ALKALOIDS, ETC., UNDER CONSIDERATION IN SOLUTIONS WHICH MAY CONTAIN ALL OF THESE SUBSTANCES.

§ 287.

1. Acidify the solution with hydrochloric acid, add pure ether, free from alcohol, shake, separate the layer of ether, and allow it to evaporate in a glass dish.

a. NO RESIDUE REMAINS: absence of digitalin (German *) and picrotoxin. Pass on to 2.

b. A RESIDUE REMAINS: digitalin and picrotoxin may be suspected. Repeat the extraction of the aqueous liquid with ether, in order to remove as completely as possible whatever is soluble in that solvent in acid solution, and

* The French product would have to be brought into solution with chloroform, into which, however, narcotin, if present, would also go.

let the ether evaporate. Proceed with the aqueous residue according to 2, and treat the residue of the ether solution, which may contain traces of atropin, as follows:

α. Dissolve a portion in alcohol, and allow the solution to evaporate slowly. Long silky needles radiating from a point indicate PICROTOXIN. Confirm according to the reactions given in § 285.

β. Dissolve a portion in concentrated sulphuric acid, and add bromine solution. A more or less pure purple color indicates DIGITALIN.

γ. Traces of ATROPIN can be recognized most certainly by the dilating action of the aqueous solution of the residue upon the pupil of the eye.

2. To a portion of the aqueous solution add a solution of iodine in potassium iodide, and to another portion add some phosphomolybdic acid.

a. A PRECIPITATE IS PRODUCED IN BOTH CASES: alkaloids are indicated. Pass on to 3.

b. NO PRECIPITATE IS PRODUCED IN EITHER CASE: the absence of alkaloids is indicated. Pass on to test for salicin according to § 283.

3. To a small portion of the aqueous solution add solution of caustic potash or soda till just alkaline, observe whether a precipitate is produced, then add more caustic potash or soda solution in large excess, and, after long standing, dilute with some more water.

a. NO PRECIPITATE WAS PRODUCED BY POTASSIUM OR SODIUM HYDROXIDE, OR A PRECIPITATE SO PRODUCED HAS REDISSOLVED: presence of atropin, morphin, or cocain, and absence of all other alkaloids. Mix a fresh portion of the neutralized aqueous solution with sodium bicarbonate in excess, stir, and allow it to stand for some time.

α. NO PRECIPITATE IS PRODUCED: absence of morphin. Mix a portion of the aqueous liquid with sodium hydroxide in excess, shake the liquid, which has remained clear or has become clear again, with ether, and find whether the latter leaves a residue of ATROPIN upon evaporation (§ 281, 6, 8, 9). Shake another portion of the acid solution with amyl alcohol, and find if this leaves COCAIN upon evaporation (§ 272, 9).

β. A PRECIPITATE IS PRODUCED: MORPHIN. Filter it off, and test it further according to § 271, 7, 8, and 9. To test for atropin and cocain, proceed according to *α* with new portions of the original solution which has been extracted with ether.

b. A PRECIPITATE WAS PRODUCED BY CAUSTIC POTASH OR SODA, WHICH WOULD NOT DISSOLVE IN EXCESS OF THE PRECIPITANT, EVEN AFTER STANDING FOR SOME TIME, AND BY MODERATE DILUTION. Treat the larger part of the acidified aqueous fluid like the small portion above, and filter. Proceed with the precipitate according to 4. Shake the alkaline filtrate with ether, allow it to stand for an hour (so that the morphin which has at first dissolved in the ether may separate again as completely as possible), and separate the ether from the aqueous solution. Allow the ether to evaporate, and test the residue for ATROPIN according to § 281, 6, 8, 9. Separate any MORPHIN from the aqueous layer by carbonic acid (§ 271, 4), and test it further according to § 271, 7, 8, and 9. Test a new portion of the original acid solution for COCAIN by shaking with amyl alcohol (see *a*, *α*).

4. Wash the precipitate filtered off in 3, *b*, with cold water, dissolve it in a slight excess of dilute sulphuric acid, add solution of sodium bicarbonate till the fluid is neutral, stir actively, rubbing the sides of the vessel, and allow to stand for an hour.

a. NO PRECIPITATE IS FORMED: absence of narcotin and cinchonin. Boil the solution nearly to dryness, and take up the residue with cold water. If nothing insoluble remains, pass on to 6; but if a residue does remain, examine it by 5 for quinin (of which a small amount may be present), strychnin, brucin, and veratrin.

b. A PRECIPITATE IS FORMED. (This may contain narcotin, cinchonin, and quinin, compare § 286, 3, *b*). Filter, proceeding with the filtrate according to *a*, and with the precipitate as follows: Wash it with cold water, dissolve in a little hydrochloric acid, add ammonia in excess, and then a not too small quantity of ether containing about 2 per cent of alcohol.

α. THE PRECIPITATE HAS COMPLETELY DISSOLVED IN

in general, in order that they may not be confused with the vegetable alkaloids, as has often happened. This may occur easily, if the analyst allows himself to be misled into concluding that some vegetable alkaloid is present on the strength of single reactions, for there are ptomains of many different kinds, and especially some which show a marked similarity to certain vegetable alkaloids as far as single reactions are concerned. For actual chemico-legal investigations, therefore, works must be used which, on the one hand, take into consideration all, or almost all, of the alkaloids, etc., or which, at least, treat the poisonous ones in a comprehensive manner, and which, on the other hand, consider the ptomains.*

1. STAS'S METHOD † FOR THE DETECTION OF POISONOUS ALKALOIDS (AND OF DIGITALIN AND PICROTOXIN), MODIFIED BY J. AND R. OTTO.‡

§ 288.

STAS'S process depends upon the following facts:

α. The acid salts of the alkaloids are soluble in water and alcohol.

β. The normal and acid salts of the alkaloids are generally insoluble in ether. Hence, salts of the alkaloids

* See especially the following: FR. JUL. OTTO'S "Anleitung zur Ausmittelung der Gifte," 6te Aufl., von ROB. OTTO, Braunschweig (Fr. Vieweg und Sohn), 1884 (considers also the ptomains comprehensively); DRAGENDORFF, "Beiträge zur gerichtlichen Chemie einzelner organischer Gifte," St. Petersburg (Schmitzdorff), 1872; DRAGENDORFF, "Beiträge zur gerichtlichen Chemie," St. Petersburg (Wienecke), 1884; DRAGENDORFF, "Gerichtlich-chemische Ermittelung von Giften," 3te Aufl., Göttingen (Vandenhoeck und Ruprecht), 1888; SONNENSCHEIN, "Handbuch der gerichtlichen Chemie," 2te Aufl. bearbeitet von CLASSEN, Berlin (Hirschwald), 1881. In addition, a very great number of treatises deal particularly with ptomains, in regard to which I refer to my "Zeitschrift für analytische Chemie," as well as to the articles of BECKURTS, Chem. Centralbl., 1886, p. 894; JESERICH, *ibid.*, 1889, II, p. 617; and CIOTTO and SPICA, *ibid.*, 1890, II. p. 978.

† Bull. de l'Académie de Médecine de la Belgique, **9**, 304; Jahrb. f. prakt. Pharm., **24**, 313; Jahresb. von LIEBIG u. KOPP, 1851, 640.

‡ Annal. d. Chem. u. Pharm., **100**, 44; FR. JUL. OTTO'S "Anleitung zur Ausmittelung der Gifte," 6te Aufl., von ROB. OTTO, p. 105 *et seq.* Cocain is not taken into consideration in this process. In regard to a modification of it, relating to the detection of cocain, compare MUSSI, Zeitschr. f. analyt. Chem., **28**, 384.

do not usually pass into ethereal solution when the neutral or acid solution is shaken in ether, and hence also the alkaloids pass into aqueous solution as acid sulphates when the ethereal solution of the pure alkaloid is shaken with dilute sulphuric acid.

γ. If aqueous solutions containing the normal or acid salts of alkaloids are mixed with caustic, carbonated, or bicarbonated alkalies, the alkaloids are liberated, and if ether or amyl alcohol is now added, and the mixture is shaken, the pure alkaloids pass into solution in the solvent.

It will be evident from what follows that there are certain exceptions to these general rules:

a. If alkaloids are to be looked for in the contents of a stomach or intestines, in food, or generally in pappy matters, mix the substance with twice its weight of strong pure alcohol,* and just enough tartaric acid to give a decided reaction (the addition of more than this is to be avoided), and warm to 70° or 75° with the use of a return-condenser. Allow the mixture to cool thoroughly, filter, and wash with strong, pure alcohol.

If the heart, liver, lungs, or similar organs are to be dealt with, cut them up fine, moisten with the acidified alcohol, squeeze, repeat the operation till the substance is exhausted, and filter the mixed fluids.

b. Evaporate the alcoholic fluids at a rather low temperature. This may be done in a porcelain dish on a water-bath, keeping the water not warmer than 80°. The temperature of the solution under these circumstances will not rise higher than 40° or 50°. If this temperature is considered too high, hasten the evaporation by blowing air across the surface of the solution. STAS considers that the temperature should not exceed 35°; and he therefore evaporates under a bell-glass over sulphuric acid, with or without the aid of an air-pump, or in a retort with a current of air passing through it. Such extreme caution, however, is very rarely necessary; at all events, the

* This is to be rectified with the addition of some tartaric acid, in order to free it from alkaloidal substances (R. OTTO).

principal part of the fluid may be always evaporated off on a gently heated water-bath.

If insoluble substances separate on evaporation (fat, etc.), as is usually the case, filter the now aqueous fluid through a moistened filter, and evaporate the filtrate and washings, as described above, to the consistence of an extract. If no insoluble substances separate on evaporating the alcoholic fluid, it may be, of course, at once evaporated to the consistence of an extract.

c. In order to make complete extraction possible, to the residue left on evaporation add gradually small portions of cold absolute alcohol, mix intimately, and finally add a larger quantity of alcohol, in order to separate everything that can be precipitated by it. Filter the alcoholic extract through a filter moistened with alcohol, wash the residue with cold alcohol, evaporate the alcoholic solution at a low temperature (see above), take up the residue with a little water, neutralize the greater part of the free acid with dilute caustic soda, leaving the solution faintly but *distinctly acid*, and shake with pure ether, free from alcohol, fusel-oil, etc. (§ 23). By the aid of a separating-funnel, or a burette with a glass stopcock, separate the ether from the aqueous layer, and repeat the extraction of the acid aqueous solution with ether until the last ether extracts are no longer colored. Of the alkaloids, etc., taken into consideration here, the ether takes up, besides coloring matters, picrotoxin and digitalin (German, compare the foot-note on p. 715), and also traces of veratrin and atropin. It is advisable to keep the first, strongly colored ethereal extract apart from the subsequent ethereal washings, so that they may be examined separately (compare *h*).

d. Gently warm the aqueous, acid solution which has been separated from ether, to remove the dissolved ether, and add solution of caustic soda cautiously, till the fluid gives a distinct reaction with turmeric-paper. The alkaloids are thus liberated, morphin * dissolving in the

* Concerning the various reactions of morphin, oxydimorphin, apomorphin, and codeïn, compare M. Marmé, Zeitschr. f. analyt. Chem., **24**, 642, and Donath, Hesse, and Polstorff, *ibid.*, **26**, 743.

excess of sodium hydroxide. Shake the fluid with pure ether, and after an hour separate the two layers of fluid, as in *c*. The ethereal extract contains the whole of the alkaloids, except morphin, only a small part of which dissolves in it. The amount of morphin dissolved by the ether is the smaller the more completely the acidified aqueous solution was freed from dissolved ether, and the longer the time which was allowed to elapse between the shaking with ether and the separation of the two layers of fluid. Allow a portion of the ethereal extract to evaporate in a large watch-glass, which should be placed upon a support heated to about 25° or 30° (to prevent condensation of water). If no residue remains, no alkaloid was dissolved in the ether. Pass on to *g*. If a residue does remain, its appearance will give some idea of the nature of the alkaloid. Thus, oily streaks, which gradually collect to a drop, and when gently warmed give an unpleasant, suffocating odor, would indicate a fluid, volatile base; while again, a solid residue, or a turbid fluid containing solid particles in suspension, would indicate a non-volatile solid base. If the ethereal extract has left a residue, repeat the treatment of the aqueous fluid with larger amounts of ether, until a portion of the last ethereal washings leaves no residue on evaporation. Allow the mixed ethereal extracts to evaporate in a small glass dish placed upon a bath containing water at about 30°, keeping the little dish filled up by the addition of fresh quantities.

The aqueous fluid which contains any morphin present is to be examined according to *g*.

e. If the acidified aqueous fluid in *c* has been well exhausted with ether, the alkaloids will remain in so pure a state on the evaporation of the ethereal extract that the tests may be applied at once to the residue. If the residue consists of oily streaks or drops, complete the evaporation in a vacuum over sulphuric acid, in order to remove the remainder of the ether and ammonia, and then test for coniin and nicotin, according to § 270. If the residue is crystalline, examine it at first under the microscope, and then test it according to § 286 or § 287, unless

the appearance of the crystals should indicate a particular alkaloid. If the residue consists of amorphous rings, dissolve it in absolute alcohol with the aid of a gentle heat, allow the solution to evaporate slowly, observe whether any crystals are thus formed, and then proceed as directed.

f. If, on the contrary, the acidified aqueous fluid in c has been insufficiently treated with ether, the residue obtained on the evaporation of the ethereal extract will not be pure enough to be tested at once. In this case dissolve in water slightly acidified with sulphuric acid, filter, if necessary, and shake repeatedly with ether (the ethereal solution may contain the remainder of the picrotoxin and digitalin, and is to be treated like the ethereal solution in c), mix the aqueous solution, after it has been freed from dissolved ether by gentle warming, with caustic potash or soda solution in decided excess, and shake repeatedly with ether, using the precautions mentioned in *d*, until the last extract leaves no residue upon evaporation. Allow the ethereal extracts to evaporate, as prescribed in *d*, and proceed with the now pure alkaloid residue according to *e**, and mix the alkaline, aqueous fluid, which may contain the remainder of the morphin, with that obtained in *d*.

g. The alkaline, aqueous liquid obtained in *d*, or in *d* and *f*, which must contain the whole or the greater part of the morphin, is treated as follows: First free it by gentle heating from the ether dissolved in it, add hydrochloric acid to acid reaction, then ammonia in excess,

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* As it appears that strychnin cannot always be obtained pure in this way, Fr. Janssens recommends (Zeitschr. f. analyt. Chem., 4, 48) mixing the solution in dilute tartaric acid, containing the foreign substances, with sufficient finely powdered sodium bicarbonate, with stirring, so that the fluid may be acidified with free carbonic acid only. If any precipitate is formed, this should be filtered off as quickly as possible. The strychnin is dissolved in the free carbonic acid, and will be precipitated by boiling the filtrate and partially evaporating it. When it has been filtered off and washed, it is dissolved in a small quantity of dilute sulphuric acid (1 : 200), potassium carbonate is added in excess, and the fluid is shaken with six times its volume of ether, which is then poured off and allowed to evaporate. Chloroform is to be preferred to ether for extracting the alkaline solution.

and without delay pure amyl alcohol,* and shake.† As morphin is decidedly more readily soluble in warm amyl alcohol than in cold, it is advisable to dip the flask into warm water. Separate the two fluids by means of a funnel, and repeat the extraction of the ammoniacal liquid with fresh quantities of amyl alcohol. Allow the united amylic extracts to evaporate, after freeing them from water completely by allowing them to settle and filtering, and test the residue, if any remains, for morphin. If the residue is not pure enough, dissolve it in water acidified with sulphuric acid, filter, shake with warm amyl alcohol, mix the aqueous fluid with ammonia, and shake the alkaline solution with amyl alcohol. On evaporating this amylic extract, after freeing it from water, the morphin will remain pure, and is to be tested further according to § 271. In order to purify morphin, SCHEIBE prefers, after shaking the sulphuric acid solution of it with amyl alcohol, to add to the former a layer of a mixture of 10 parts of anhydrous ether and 1 part of 95 per cent alcohol, then to add ammonia, and extract by shaking. Upon evaporating the ether-alcohol, morphin remains behind.

h. The ethereal extracts obtained in *c*, or in *c* and *f*, have now to be tested for picrotoxin and digitalin. The extracts also contain coloring matters, etc., which are principally present in the first portions. It is therefore advisable, following OTTO's advice, to evaporate the first, strongly colored portions apart from the subsequent portions, and to examine the residues separately. Moisten them with glacial acetic acid, warm with water, and filter the solutions from the insoluble matter, which generally has a resinous character. Then extract any PICROTOXIN and DIGITALIN that may be present in the acid solutions by shaking with chloroform. Any traces of ATROPIN, which

* In regard to the necessary purification of the amyl alcohol to be used, compare HAITINGER, also W. LENZ, Zeitschr. f. analyt. Chem., **22**, 637.

† STAS recommended ether alone for the extraction of alkaloids, while L. v. USLAR and J. ERDMANN (Annal. d. Chem. u. Pharm., **120**, 121, and **122**, 360) prefer the use of amyl alcohol only. However, it is generally best to employ both solvents in succession, as directed in the text.

might be present here (compare § 287, 1), are finally obtained by adding an excess of ammonia to the acid, aqueous liquid which has been separated from the chloroform, and shaking out with benzol. Upon careful evaporation of the chloroform and the benzol extracts, the substances contained in them remain behind, and are to be examined further.

2. Dragendorff's Method.*

§ 289.

The method elaborated by Dragendorff, and gradually made more and more perfect by him, embraces a very large series of alkaloids and also takes many other organic substances into consideration. This is given here in its outlines, and applied to the alkaloids, etc., which are here taken into consideration. It should be stated that care must be taken to carry out the separation of the liquids used for extraction in such a manner that they may be free from all water, when evaporated, it being most advantageous to separate them by means of a burette provided with a glass stop-cock. It should be added that the evaporations are to be effected at a relatively low temperature. If a solvent leaves a residue upon evaporation, the extraction is then to be repeated until the last extract no longer leaves a residue worth mentioning. The method includes the following operations:

a. Extraction with water at 40 or 50°, after the addition of dilute sulphuric acid to distinct acid reaction.

b. Concentration of the aqueous extract to the consistence of syrup,† maceration of the residue with three or four volumes of alcohol for 24 hours at 30°, cooling and filtering, and washing with alcohol of 70 per cent by volume.

c. Removal of the alcohol by distillation, filtration of

* "Die gerichtlich-chemische Ermittelung von Giften," 3te Aufl., Göttingen (Vandenhoeck und Ruprecht), 1888, p. 137 *et seq.*

† If the presence of decomposable alkaloids, like morphin, cocain, etc., is suspected, it is better to omit the evaporation of the acid extract, and to mix this at once with four or five volumes of alcohol, in order to carry on the operation from this point according to *b*.

the entirely cooled residue from the distillation after diluting it with some water, if necessary.

d. Extraction of the acid, aqueous solution by shaking with freshly rectified petroleum-ether. (None of the alkaloids, etc., considered here go into this extract.)

e. Extraction of the acid, aqueous solution, by shaking with benzol. Digitalin (in the narrower sense), and also traces of veratrin, go into solution in benzol.

f. Extraction of the acid, aqueous solution, by shaking with chloroform. By this are dissolved—cinchonin,* picrotoxin, digitalein, and also traces of narcotin, brucin, and veratrin.

g. Extraction of the acid, aqueous solution (separated from chloroform), by shaking with petroleum-ether, in order to remove the remainder of the chloroform.

h. Supersaturation of the aqueous solution with ammonia, extraction of the ammoniacal liquid by shaking with petroleum-ether in the cold, and separating this liquid after long standing. Under these circumstances, coniin and nicotin, as well as small amounts of strychnin, brucin, veratrin, and quinin, and also a part of the cocain, go into the petroleum-ether.

i. Extraction of the ammoniacal, aqueous solution with benzol. (If the layer of benzol appears gelatinous, separate the jelly as far as possible from the water, place it upon a dry filter, cover the funnel with a plate of glass, and, after a few hours, press the jelly with a glass rod. Clear, liquid benzol is then separated.) Strychnin, brucin, quinin, cinchonin, atropin, veratrin, narcotin, and the rest of the cocain pass into the benzol.

k. Extraction of the ammoniacal, aqueous solution, by shaking with chloroform. The remainder of the cinchonin and a minute amount of morphin are thus extracted.

l. Extraction of the ammoniacal, aqueous solution with amyl alcohol. Morphin and salicin are obtained in solution.

m. Evaporation of the ammoniacal, aqueous solution with the addition of powdered glass; extraction of the

* According to my own experiments, no cinchonin is dissolved.

dry residue with chloroform. This operation is not necessary for the bodies that are here taken into consideration, because none of them are left.

It is easy to see that the methods described in §§ 288 and 289 may be modified in various ways, and that they may be greatly simplified when the object in view is exactly defined, *e.g.*, when it is required to detect morphin in urine, or to discover strychnin in a sample of food. Such modifications, therefore, have been recommended in large numbers, but, in regard to them, I must refer to my "Zeitschrift für analytische Chemie," * and I will add here only a few methods which depend upon entirely different principles.

3. Sonnenschein's Method.†

§ 290.

Extract the substance with water which has been strongly acidified with hydrochloric acid, evaporate the extract at 30° to the consistence of a thin syrup, dilute with water, allow the mixture to cool for a long time, filter, and add phosphomolybdic acid to the filtrate. After allowing it to settle for a considerable time, filter the precipitate containing all the alkaloids (but not digitalin, picrotoxin, and salicin), wash it with

* Compare also Cushman, Chem. Centralbl., 1894, II, p. 461 (deals with the detection of strychnin in parts of dead bodies); Wormley, *ibid.*, 1890, II, p. 565 (concerning the detection of morphin in urine); Sestini and Campani, *ibid.*, 1892, I, p. 184 (concerning the detection of quinin in urine); Lindemann and Motteu, Pharmac. Centralhalle, 1893, p. 524 (concerning the detection of strychnin in beer, milk, etc., of morphin in beer and urine, and of quinin in beer). A few other more recent treatises should also be referred to here, which relate closely to the subject under consideration: Alt, Pharmac. Centralhalle, 1889, p. 484 (concerning the question as to the parts of the body in which injected morphin is present); Lamal, *ibid.*, 1889, p. 216 (concerning the conversion of morphin into oxymorphin in the organism); Noyes, Chem. Centralbl., 1894, I, p. 699, and Ipsen, Pharmac. Centralhalle, 1894, p. 418 (concerning the power of resistance of strychnin to putrefaction); Sonnié Moret, Chem. Centralbl., 1893, I, p. 859, and Glasenap, *ibid.*, 1894, II, p. 220 (concerning the changes which cocain undergoes in the organism).

† Sonnenschein, "Handbuch der gerichtlichen Chemie," 2te Aufl., bearbeitet von Classen, Berlin (Hirschwald), 1881, p. 312.

water to which some phosphomolybdic acid and nitric acid have been added, and rinse it into a flask. After adding barium hydroxide to alkaline reaction, connect the flask with a condenser, and a receiver containing some hydrochloric acid and connected with a PÉLIGOT'S tube, and heat to boiling for a considerable time. Ammonia and volatile bases escape, and unite with the hydrochloric acid in the receiver. Precipitate the excess of barium hydroxide in the residue from the distillation, by means of carbonic acid, evaporate to dryness, treat with strong alcohol, filter, and allow the filtrate to evaporate. If the alkaloids remaining behind are not yet pure enough, they are to be purified by one of the methods given in §§ 288 or 289. If glue is present, which is also precipitated by phosphomolybdic acid, a suitable means of purification would be to dissolve the impure alkaloid in water with the addition of some hydrochloric acid, and to carry out a separation by dialysis, according to method 4.

4. SEPARATION BY DIALYSIS.

§ 291.

The dialytic method devised by GRAHAM, and described in § 8, may also be advantageously employed to effect the separation of alkaloids from the contents of the stomach, intestines, etc. Acidify with hydrochloric acid, and place the matter in the dialyzer. The alkaloids, being crystalloids, penetrate the membrane, and are found, for the greater part, after 24 hours, in the outer fluid; from this they may, then, according to circumstances, either be thrown down at once, after concentration by evaporation, or they may be further purified by one of the methods described above.

5. METHOD USED BY GRAHAM AND A. W. HOFMANN* FOR DETECTING STRYCHNIN IN BEER.

§ 292.

This method, which is based on the known fact, that a solution of a salt of strychnin, when mixed and shaken with

* Annal. d. Chem. u. Pharm., 83, 39.

animal charcoal, yields its strychnin to the charcoal, will undoubtedly be found applicable also for the detection of other alkaloids. The process is conducted as follows:

Shake the aqueous, neutral, or slightly acid liquid with animal charcoal (GRAHAM and HOFMANN used 30 g to the liter), let the mixture stand for from 12 to 24 hours, with occasional shaking, filter, wash the charcoal twice with water, then boil for half an hour with alcohol of 80 or 90 per cent, using about four times as much as the quantity of charcoal taken, and avoiding, by an appropriate arrangement, loss of alcohol by evaporation. Filter the alcohol hot from the charcoal, and distil the filtrate; add a few drops of solution of caustic potash to the residual, watery fluid, shake with ether (or better still with chloroform), and separate the solvent from the aqueous liquid. Upon spontaneous evaporation, this leaves the strychnin in a state of sufficient purity to admit of its further examination by reagents (see § 278).

MACADAM * employed the same method in his numerous experiments to detect strychnin in the bodies of dead animals. He treated the comminuted matters with a dilute aqueous solution of oxalic acid in the cold, filtered through muslin, washed with water, heated to boiling, filtered still warm from the coagulated albuminous matters, shook with charcoal, and proceeded in the manner just described. According to his statements, the residue left by the evaporation of the alcoholic solution was generally at once fit to be tested for strychnin. Where it was not so, he treated the residue again with solution of oxalic acid, and repeated the process with animal charcoal.†

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* Pharm. Journ. Trans., XVI, 120, 160, LIEBIG and KOPP, Jahresbericht, 1856, p. 759.

† In regard to other methods of procedure differing essentially from those given above, compare CHANDELON, Zeitschr. f. analyt. Chem., 24, 485; KOBERT, *ibid.*, 30, 755, KÜSTER and HILGER, Chem. Centralbl., 1889, II, p. 717; HILGER and JANSEN, *ibid.*, 1894, I, pp. 114 and 282.

APPENDIX II.

General Plan of the Order in which Substances should be analyzed for Practice.

§ 293.

When the student has made himself familiar with the deportment of bodies to reagents, and has learned by practice how the metals and acids belonging to different groups, and also the members of one and the same group, may be separated from one another and recognized by the aid of regeants, he proceeds to make actual investigations, in order to learn qualitative chemical analysis. In analyzing for the sake of practice, it is not a matter of indifference whether the student follows no rule or order whatever in the selection of the substances which he intends to analyze, or whether, on the contrary, his investigations and experiments proceed systematically. Many ways, indeed, may lead to the desired end, but one of them will invariably prove the shortest. I will, therefore, here point out a course which experience has shown to lead safely and speedily to the attainment of the object in view.

When analyzing for the sake of practice only, the student must above all things possess the means of verifying the results obtained by his experiments, for it is only in this way that confidence is established in the certainty of the operation, and a positive reliance, a necessary self-confidence, is awakened. It is only from such a course that he becomes convinced that the end is attained only by a regular and well-planned process. The substances to be examined should, therefore, be mixed by another person who knows their exact composition. If there is no opportunity for doing this, it is better that the student should mix them for himself, and then detect the constituents exactly as if he did not know them,

rather than that he should choose entirely unknown substances for examination. If a beginner is given a substance to analyze, the constitutents of which are not exactly known, there is no doubt that he will find something, but he will gain little confidence in the method or in his own ability if his instructor is obliged to answer him, "It is quite possible," or "It may be so," and is unable to say "Yes" or "No."

According to his individuality and his previous preparation, one student will be obliged to make a large number of investigations, while another will require a smaller number, before he understands the subject. The following plan of one hundred examples is given, because I am convinced that such a number of appropriately chosen analyses is sufficient, on the average, for learning the process thoroughly.

A. *From* 1 *to* 20.

AQUEOUS SOLUTIONS OF SIMPLE SALTS, *e.g.*, sodium sulphate, calcium nitrate, cupric chloride, etc. These investigations will serve to teach the student the method of analyzing substances soluble in water, which contain but one metal. In these examples, it is only intended to ascertain what metal is present in the fluid under examination; and neither the detection of the acid nor the proof of the absence of all other metals besides the one detected is required.

B. *From* 21 *to* 50.

SALTS, ETC., CONTAINING ONE METAL AND ONE ACID, ETC., IN THE SOLID STATE (in form of powder), *e.g.*, barium carbonate, sodium borate, calcium phosphate, arsenious oxide, sodium chloride, hydrogen potassium tartrate, cupric acetate, barium sulphate, lead chloride, etc. These analyses will serve to teach the student how to make a preliminary examination of a solid substance by heating in a tube and before the blowpipe; how to convert it into a proper form for analysis, *i.e.*, how to dissolve or decompose it; how to detect *one* metal, even in substances *insoluble* in water; and how to demonstrate the presence of *one* acid. The detection of both the metal and the acid is required, but it is not necessary to prove that no other bodies are present. These examples induce more

acute observation, and give occasion for deeper reasoning, because the observations made in the preliminary testing, the behavior of the substance towards solvents, and the knowledge of the metal present, lead to the consideration of the acids for which it is necessary to test.

C. *From* 51 *to* 65.

AQUEOUS OR ACID SOLUTIONS OF SEVERAL METALS. These investigations will serve to teach the student the method of separating and distinguishing several metals from each other. The proof is required that no other metals are present besides those detected. No regard is paid to the acids.

D. *From* 66 *to* 80.

DRY MIXTURES OF EVERY DESCRIPTION. A portion of the salts should be organic, another inorganic; a portion of the compounds, soluble in water or hydrochloric acid, another insoluble, *e.g.*, mixtures of sodium chloride, calcium carbonate, and cupric oxide,—of magnesium ammonium phosphate, and arsenious oxide,—of calcium tartrate, calcium oxalate, and barium sulphate,—of sodium phosphate, ammonium nitrate, and potassium acetate, etc.

These investigations will serve to teach the student the preliminary examination of complex substances; how to treat mixtures of different substances with solvents; how to detect several acids in presence of each other; how to detect the metals in presence of phosphates, oxalates, etc., of the alkali-earth metals; and they will also serve as a general introduction to scientific and practical analysis. All the component parts must be detected, and the nature of the substance ascertained.

E. *From* 81 *to* 100.

NATIVE COMPOUNDS, ARTICLES OF COMMERCE, ETC. Mineral and other waters, minerals of every description, soils, ashes of plants, potash, soda, alloys, colors, etc.

APPENDIX III.

Record of the Results of the Analyses performed for Practice.

§ 294.

The manner in which the results of analytical investigations, made for practice, ought to be recorded is not a matter of indifference, and although any way of recording may answer the purpose, some methods are better adapted than others for rapidly impressing the subject upon the mind, and inducing, quickly but thoroughly, a comprehension of the whole field.

The following examples will serve to illustrate the method which I have found the most suitable and convenient in this respect:

Plan of Recording the Results of Experiments, Nos. 1–20.

Colorless fluid of neutral reaction.

HCl,	H_2S,	$(NH_4)_2S$,	$(NH_4)_2CO_3$
no precipitate,	*no precipitate,*	*no precipitate,*	and NH_4Cl,
consequently no	no Pb	no Fe″	*a white precipitate,*
Ag	" Hg″	" Mn	consequently ei-
Hg′	" Cu	" Ni	ther Ba, Sr, or
	" Bi	" Co	Ca. No precipi-
	" Cd	" Zn	tate by solution
	" As	" Al	of $CaSO_4$, conse-
	" Sb	" Cr	quently CALCIUM.
	" Sn		
	" Au		
	" Pt		
	" Fe‴		

PLAN OF RECORDING THE RESULTS OF EXPERIMENTS, NOS. 21–50.

White powder, fusing in the water of crystallization upon application of heat, then remaining unaltered. Glows when heated before the blowpipe upon charcoal. The $NaPO_3$ bead is not colored by it, and remains clear upon cooling. Soluble in water. Reaction neutral.

HCl,	H_2S,	$(NH_4)_2S$,	$(NH_4)_2CO_3$	$HNaNH_4PO_4$ and
no ppt.	*no ppt.*	*no ppt.*	and NH_4Cl, *no ppt.*	NH_4OH, *a white, crystalline ppt.* consequently MAGNESIUM.

The detected metal being Mg, and the analyzed substance being soluble in water, the acid radical can only be Cl, I, Br, SO_4, NO_3, etc. The preliminary examination has proved the absence of the organic acids and of nitric acid.

$BaCl_2$ produces a white precipitate, which HCl fails to dissolve; consequently SULPHURIC ACID.

PLAN OF RECORDING THE RESULTS OF EXPERIMENTS, NOS. 51–100.

A white powder, which on heating in a glass tube acquires a permanent yellow tint, gives no sublimate, emits no visible fumes nor any vapors having an acid or alkaline reaction. Before the blowpipe, a malleable metallic globule, and yellow incrustation, with white border upon cooling. Insoluble in water, effervesces with HCl, incompletely soluble in that acid, readily soluble in HNO_3 to a colorless fluid.

HCl,	H_2S,	$(NH_4)_2S$,	$(NH_4)_2CO_3$ and NH_4Cl,	$HNaNH_4PO_4$	No fixed	$Ca(OH)_2$,
white ppt., insoluble in an excess, completely soluble in hot water; H_2SO_4 producing a white ppt. in the solution: LEAD.	black ppt., insoluble in $(NH_4)_2S_x$, readily soluble in HNO_3. H_2SO_4 produces a white ppt.: LEAD. Examination for Cu, Bi, and Cd, results negative.	white ppt. NH_4OH, applied by itself, produces no ppt.; solution of ppt. in HCl remains clear upon addition of caustic soda in excess	white ppt., dissolved in HNO_3 and evaporated to dryness. C_2H_4OH and $(C_2H_5)_2O$ extract gives with H_2SO_4 no ppt.: no calcium. Residue dissolved in H_2O, with K_2CrO_4 in presence of $HC_2H_3O_2$ no ppt.: no barium. NH_4OH and $(NH_4)_2CO_3$, white ppt.: STRONTIUM.	and NH_4OH, no ppt.: No magnesium.	residue upon evaporation. No alkali metals.	has failed to evolve NH_3.
		HCl then NH_4OH, no ppt. | H_2S, white ppt.: ZINC.				

Of the acids, CARBONIC ACID has already been found. Of the remaining acids, the following cannot be present:

The preliminary examination has proved the absence of organic acids and HNO_3.

$HClO_3$ cannot be present, because the substance is entirely insoluble in water.

S and H_2SO_4 not, because the substance is readily soluble in HNO_3.

H_2CrO_4 not, as the substance is readily soluble in HNO_3, and as the nitric acid solution is colorless.

H_3PO_4, H_2SiO_3, HF, and $H_2C_2O_4$ not, because the solution filtered from PbS was not precipitated by simple addition of NH_4OH.

H_3BO_3 might be present in trifling quantity; the examination for it gave a negative result.

CN might be present as zinc cyanide, and Cl, I, Br in the form of basic lead compounds. However, $AgNO_3$ produced no ppt. in the nitric acid solution; accordingly, they cannot be present.

The substance contains, therefore, { metals: LEAD, ZINC, STRONTIUM. / acids: CARBONIC ACID.

APPENDIX IV.

Table of Solubilities.

Showing the classes to which the compounds of the commonly occurring elements belong in respect to their solubility in water, hydrochloric acid, nitric acid, or aqua regia.

§ 295.

Preliminary Remarks.

For the sake of brevity, the classes to which the compounds belong, according to the division made in § 214, are expressed by letters. These have the following signification:

W or w, soluble in water.

A or a, insoluble in water, but soluble in hydrochloric acid, nitric acid, or in aqua regia.

I or i, insoluble in water, hydrochloric acid, or nitric acid.

Further, substances standing on the border-lines are indicated as follows:

W—A or w—a, difficultly soluble in water, but soluble in hydrochloric acid or nitric acid.

W—I or w—i, difficultly soluble in water, the solubility not being greatly increased by the addition of acids.

A—I or a—i, insoluble in water, difficultly soluble in acids.

If the behavior of a compound to hydrochloric and nitric acids is essentially different, this is stated in the notes.

Capital letters indicate common substances used in the arts and in medicine, while the small letters are used for those less commonly occurring.

The salts are generally considered as normal, but basic and acid salts, as well as double salts, in case they are important in medicine or in the arts, are referred to in the notes.

The small numbers in the table refer to notes on the following pages.

SOLUBILITY

	Potassium.	Sodium.	Ammonium.	Barium.	Strontium.	Calcium.	Magnesium.	Aluminium.	Chromium.	Zinc.	Manganese.	Nickel.	Cobalt.
Oxide.....	W	W	W	W	w	W–A	A	A	A & I	A	a_{17}	A	A
Chromate..	W_1	w	w	a	w–a	w–a	w		a	w	w	a	a
Sulphate ..	$W_{13\cdot15}$	W	$W_{14\cdot20\cdot30}$	I	I	W–I	W	$W_{13\cdot14}$	W & I_{15}	W	W	W	W
Phosphate.	w	W_8	$w_{8\ 12}$	a	a	A_{11}	a_{12}	a	a	a	a	a	a
Borate.....	w_2	w_9	w	a	a	a	w–a	a	a	a	a	a	a
Oxalate....	W_2	W	W	a	a	A	a	a	w–a	a	w–a	a	a
Fluoride...	w	w	W	w–a	w–a	A–I	a–i	w	w	w–a	a	w–a	w–a
Carbonate.	W_4	W_{10}	W	A	A	A	A			A	A	A	A
Silicate ...	W	W		a	a	a	a	a–i	a	a	a	a	a
Chloride...	W_{27}	W_{25}	$W_{21\cdot38}$	W	W	W	W	w	W & I	W	W	W	W
Bromide...	W	W	w	w	w	w	w	w	w & i	w	w	w	w
Iodide.....	W	w	W	w	w	w	w	w	w	w	w	w	w
Cyanide....	W	w	w	w–a	w	w	w		a	A	a	a–i	a–i
Ferrocy'de	W	w	w	w–a	w	w	w			A–I	a	i	i
Ferricy'de.	W	w	w			w	w			a	i	i	i
S'phocy'de	W	w	W	w	w	w	w		w	w	w	w	w
Sulphide...	W	W	W	W	w	W–A_{45}	a	a	a–i	A_{16}	A	a_{18}	a_{19}
Nitrate	W	W	W	W	W	w	w	w	W	w	w	w	W
Chlorate...	W	w	w	w	W	w	w	w	w	w	w	w	w
Tartrate...	$W_{5\cdot6\cdot7\cdot22\cdot46}$	W_7	w_6	a	a	A	w–a	w	w	a	w–a	a	w
Citrate	w	w	w	a	a	w–a	w	w	w	w–a	a	w	w
Malate	w	w	w	w & a	w	w–a_{47}	w	w		w	w		
Succinate..	w	w	w	w–a	w–a	w–a	w	w–a		w–a	w	w	w–a
Benzoate ..	w	w	w	w		w	w				w		
Salicylate .	w	W	W	w–i	w–a	w–a	w						
Acetate....	W	W	W	W	w	W	w	W	w	W	w	w	w
Formate...	w	w	w	w	w	w	w	w	w	w	w	w	w
Arsenite...	W	w	w	a	a	a	a				a	a	a
Arsenate ..	W	W	w	a	a	a	a	a	a	a	a	a	a

TABLE.

Ferrous.	Ferric.	Silver.	Lead.	Mercurous.	Mercuric.	Cupric.	Bismuth.	Cadmium.	Gold.	Platinum.	Stannous.	Stannic.	Antimonious.	
a	A	a	A_{24}	A	A	A	a	a		a	a	a & i	A_{42}	Oxide
	w	a	A-I	a	w-a	w	a	a			a		a	Chromate
W_{30}	W	W-A	A-I	w-a	w_{27}	W_{30}	w	W		w	w		a	Sulphate
a	A	a	a	a	a	a	a	a			a	a	w-a	Phosphate
a	a	a	a			a	a	w-a			a			Borate
a	a	a	a	a	a	a	a	a		w	a	w	a	Oxalate
w-a	w	w	a		w-a	a	w	w-a			w	w	w	Fluoride
A		a	A	a	a	A	a	a						Carbonate
a	a		a			a		a						Silicate
W	W_{21}	I	W-I	A-I	W_{28}	W	W-A_{32}	W	W_{35}	$W_{27\cdot36}$	W	W_{46}	W-A_{43}	Chloride
w	w	i	w-i	a-i	w	w	w-a	W	w	w			w-a	Bromide
W	w	i	W-A	A	A	w	a	W	a	i	w	w	w-a	Iodide;
a-i		I	a		W	a		a	W	w				Cyanide
i	I	i	a			i					i	i		Ferrocyanide
I	w	i	w-a								i			Ferricyanide
w	w	i	a	A	w	a		w-a		a		w		Sulphocy'de
A	a	a_{23}	A	A	A_{29}	a_{31}	a	A	a_{25}	a_{29}	a_{41}	a_{41}	$A_{44\cdot45}$	Sulphide
w	w	W	W	W_{26}	W	W	W_{34}	w		w				Nitrate
w	w	w	w	w	w	w	w	w			w			Chlorate
w-a	W_{22}	a	a	w-a	a	w	a	w-a			a		a_{46}	Tartrate
w	W	a	a	a	w-a	w		a						Citrate
	W	w-a	w-a	a	w-a	w					w	w		Malate
w-a	a	a	a	a	w-a	w		w				a		Succinate
w	a	w-a	a	a	w-a	a		w						Benzoate
		w-a	w-a			w								Salicylate
w	W	w	W_{25}	w-a	w	W_{32}	w	w			w	w		Acetate
w	W	w	w-a	w	w	w	w	w			w			Formate
a	a	a	a	a	a	A							a	Arsenite
a	a	a	a	a	a	a	a					a	a	Arsenate

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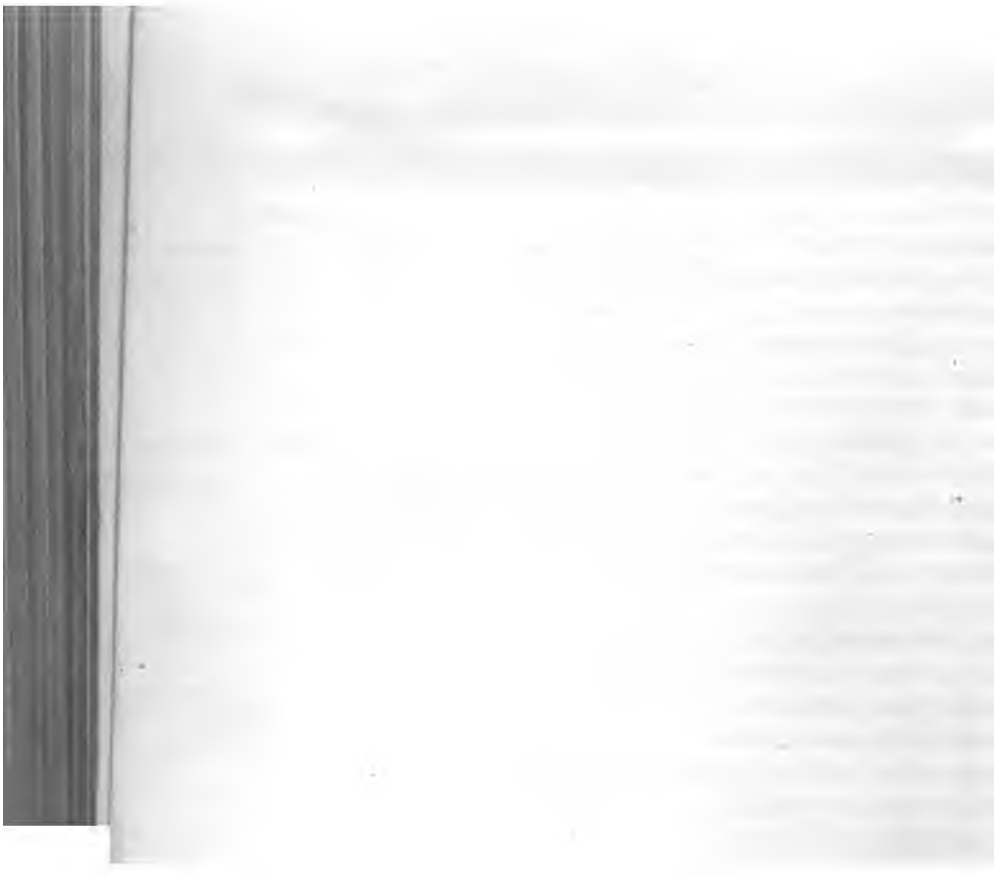
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